

Methyl and Total Mercury Spatial and Temporal Trends in Surficial Sediments of the San Francisco Bay-Delta

Assessment of Ecological and Human Health Impacts of Mercury in the
Bay-Delta Watershed

CALFED Bay-Delta Mercury Project Final Report

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EXECUTIVE SUMMARY

Recent studies indicate significant amounts of mercury are transported into the Bay-Delta from the Coastal and Sierra mountain ranges. In response to mercury contamination of the Bay-Delta and potential risks to humans, health advisories have been posted in the estuary, recommending no consumption of large striped bass and limited consumption of other sport fish. The major objective of the CALFED Bay-Delta Mercury Project “Assessment of Ecological and Human Health Impacts of Mercury in the Bay-Delta Watershed” is to reduce mercury levels in fish tissue to levels that do not pose a health threat to humans or wildlife. This report summarizes the accomplishments of the Moss Landing Marine Laboratories (MLML) and California Department of Fish and Game (CDF&G) at Moss Landing as participants in the CALFED Bay-Delta Mercury Project. Specific objectives of MLML and CDF&G include:

1. Determination of the spatial distribution of total mercury and methyl mercury in surficial sediments of the Bay-Delta. Identify locations within the Bay-Delta having high mercury methylation potentials (as indicated by the methyl mercury to total mercury ratio) (Task 4A1 & 4A2).
2. Determination of the temporal changes in total mercury, methyl mercury, and the methyl mercury to total mercury ratio at six locations within the Bay-Delta (Task 4A1 & 4A2).
3. Determination of the mercury methylation potentials in Coastal and Sierra Range river and lake sediments (Task 4A1 & 4A2).
4. Determination of the mercury methylation potential of wetland areas within the Delta (Task 4A1 & 4A2 Phase 2).

The initial survey of Bay-Delta sediments was conducted October, 1999. Samples were collected for the determination of total mercury, methyl mercury, percent Loss on Ignition (LOI), and grain size, as well as water column measurements of temperature and pH. Sediment samples were collected monthly from May, 2000 – November, 2001 at six locations in the Bay-Delta. Samples were analyzed for total and methyl mercury, and LOI. Sediment collections were made in October, 2001 from the Coastal Range and Sierra Range for the determination of mercury methylation potentials. Transects across three wetlands were conducted May 2001. Sediments were collected from the interior, middle, exterior, and control site of each wetland area for the determination of total mercury, methyl mercury, and LOI. All raw data is given in Appendix B.

Major Findings (Working Hypotheses):

- In the Bay-Delta, total mercury concentrations decreased north to south and increased east to west while methyl mercury concentrations increased north to south. The highest methyl mercury sediment concentrations were found in the

central Delta. The central Delta had the greatest mercury methylation potential when compared to the surrounding tributaries.

- Solid phase methyl mercury concentrations varied seasonally with highest concentrations occurring during late spring/summer.
- Coastal mountain streams had two orders of magnitude higher total mercury concentrations than Sierra mountain streams and the methyl mercury concentrations were equivalent. Sediments from lakes of the Coastal Range and Sierra Range were equivalent in total mercury and methyl mercury.
- Inner areas of wetlands consistently had higher solid phase methyl mercury concentrations and methyl mercury to total mercury ratios when compared to outer areas of wetlands and the control site.

INTRODUCTION

The CALFED Mercury Project – Background and Objectives

Background

Between 1850 and 1980 California was the nation's leading producer of mercury, contributing about 100 million kilograms to the world market (Churchill 2000). Most of the mercury was mined in the coast range of California. Early mercury processing using furnace volatilization of the cinnabar ore and cold surface condensation of elemental mercury was inefficient and approximately 35 million additional kilos of the metal are estimated to have been released into the Coastal Range watersheds (Churchill 2000). The mercury mined in the coast range was shipped across the central valley to the Sierra Nevada where it was used in gold mining activities. Six million kilos of mercury are thought to have been lost in placer and lode gold mining in the Sierra Nevada (Churchill 2000). Recent studies have determined that large amounts of mercury are still being transported annually into the San Francisco Bay-Delta from both the Coastal Range and the Sierra Nevada (Larry Walker and Associates 1997, Foe and Croyle 1998, Roth et al. 2001). As a result, the fish, water, and sediment of the central valley and Bay-Delta have elevated levels of mercury.

The primary human health concern of environmental mercury contamination is exposure through the consumption of contaminated fish. The dominant form of mercury in fish is the organic species methyl mercury (Bloom 1992). Methyl mercury is formed principally by sulfate-reducing bacteria in surficial sediments (Gilmour et al. 1998). Methyl mercury is readily bioaccumulated by aquatic organisms and biomagnified in the food web. Methyl mercury is a potent human neurotoxin, with developing fetuses and small children being most at risk at extremely low levels (White et al. 1995). In response to the mercury contamination of the Bay-Delta and the potential risks to humans, health advisories and interim health advisories have been posted in the estuary, recommending no consumption of large striped bass and limited consumption of other sport fish (Office of Environmental Health Hazard Assessment 1994, San Francisco Bay Regional Water Quality Control Board 1995). Elevated concentrations of mercury in fish tissue may also

represent a hazard to piscivorous wildlife. Species most at risk are fish-eating birds and mammals.

Site Description

The San Francisco Bay and Sacramento-San Joaquin Delta (Bay-Delta) is the largest estuary on the west coast of the United States. The dominant source of fresh water to the Bay-Delta is the Sacramento River with smaller contributions supplied by the San Joaquin, Mokelumne, and Cosumnes Rivers. The Cosumnes River is the only river which flows into the Bay-Delta unobstructed by dams. The Bay-Delta receives the runoff from 40 percent (60,000 sq miles) of California's land. The Bay-Delta covers 738,000 acres with hundreds of miles of waterways within its boundaries. These waterways, originally formed from the natural meandering of rivers through the marshland, are now held in place with banks made up of rip-rap armor and extensive dikes. Historic seasonal wetlands, created by the annual flooding as a result of rivers overflowing natural levees, have all but disappeared from the Bay-Delta. Large acreages of marsh habitat are now found at wildlife recreation areas and restoration sites such as the Cosumnes River Preserve (northeast delta), the Lower Sherman Island Wildlife Area (west delta), and the Yolo Bypass Wildlife Area (northwest delta). Historically, seasonal wetlands and marshes were the predominant habitat features in the central delta. Today, the majority of these seasonal wetlands have been reclaimed for agricultural uses (Nichols et al. 1986).

Much of the marshes and wetlands in the delta are constrained to the fringes of channels along rip-rap banks and narrow islands in the center of waterways (Picture 1). The subsidence of reclaimed swamp land as a result of oxidation and mechanical compaction has left much of the Bay-Delta below sea level necessitating the more than 1,000 miles of levees for protection against flooding (Picture 2).

The Bay-Delta is critical to the state of California. The Bay-Delta system is not only important as the fresh water source for 22 million Californians, but also for the crops grown in the rich delta soils as well as the habitat it provides for many fish and wildlife species.

Objectives

The present mercury project is funded by CALFED, an ambitious long-term program to improve water management in the Bay-Delta Estuary. The program includes, in addition to water management, ecosystem restoration, levee stabilization, and water quality components. The main goal of the mercury element of the water quality program is to reduce mercury concentrations in fish tissue to levels that do not pose a threat to wildlife or human health.

Organization

The CALFED Mercury Research Group consists of 15 principal investigators from State and Federal agencies, universities, private analytical laboratories, and non-profit agencies (see: <http://loer.tamug.tamu.edu/calfed>). The mercury research group is headed by Mark Stephenson of the California Department of Fish and Game (CDF&G) at Moss Landing Marine Laboratories (MLML)

MLML and CDF&G Project Objectives

MLML and CDF&G were involved with four tasks as part of the overall CALFED Mercury Research Project. A description of the tasks is briefly outlined below.

1) Spatial Patterns of Methyl Mercury Production (Task 4A1 & 4A2).

- a. Determine the spatial distribution of total mercury and methyl mercury in surficial sediments of the Bay-Delta.
- b. Use the methyl mercury to total mercury ratio to identify locations of high methylation potential.
- c. Relate spatial patterns to distributions of total mercury and percent loss on ignition (LOI)(used as a proxy for total organic carbon).

2) Temporal Patterns of Methyl Mercury Production (Task 4A1 & 4A2).

Determine the temporal changes in methyl mercury to total mercury ratios in surficial sediments at six locations within the Bay-Delta.

3) Mercury Bioavailability (Task 4A1 & 4A2 phase 2).

Compare the methylation potential of Coastal and Sierra Range sediments.

4) Methylation Efficiency of Delta Wetlands (Task 4A1 & 4A2 phase 2).

Determine the difference in methylation potential between wetland and non-wetland areas within the Delta.

METHODS

Sampling for Initial Survey (Determination of Spatial Patterns, Objective 1a-1c)

A broad scale survey of the Bay-Delta system was conducted October 10, 1999 through December 1, 1999. Ninety-six sites within the Bay-Delta (Figure 1) and one hundred fifty sites from South Bay to San Pablo Bay and the Delta tributaries were sampled within a two-month period with the majority of the Delta samples collected within the first five days. Sampling locations in South Bay and San Pablo Bay are shown in Figures 2-4. Water temperatures in the Bay-Delta at the time of sampling averaged 15 °C, and the Sacramento River was flowing at 10,000-19,000 cfs.

A geographical information system (GIS) was used to generate random sampling locations within each habitat type defined by the Wetland Inventories base map of the Bay-Delta. Once in the field, many locations were changed due to problems with access, as a result the sampling was semi-random. Table 1 gives a list of the habitat types and number of samples collected within each habitat during the Delta survey.

Sediment samples were collected remotely using the “Sludge O Matic” (SOM), a sampler designed and built at Moss Landing Marine Labs described below and in Appendix A. Samples were collected for the analysis of total mercury, methyl mercury, Loss on Ignition (LOI), and grain size (percent fines = $< 63 \mu\text{m}$).

Seasonal Sampling (Determination of Temporal Patterns, Objective 2)

Six sites within the Bay-Delta system were selected for monthly monitoring (Figure 5). The locations were selected to represent a variety of habitat types from different areas of the Bay-Delta. A position and brief description of the habitat type for each location is given in Table 2. Sampling frequency was monthly beginning May 2000 and increased to twice-monthly June 2001. Stations were located with a hand held GPS to assure re-sampling to within a few meters. Sediment was collected using the SOM sampler. The samples were analyzed for total mercury, methyl mercury, and LOI. Grain size (percent fines as described above) analysis was conducted on a selected sub-set of the samples.

Bioavailability Sampling (Objective 3)

Sediment collections were made during October, 2001 in the coastal mountain range (Cache Creek and other areas) and in the Sierra Nevada range (Cosumnes River and other areas)(Figure 6). Two seasonal lakes (Capay Dam and Cache Creek Settling Basin) were also sampled to be able to make a comparison between the permanent lakes and seasonal lakes of the coastal range. Samples were collected using a scoop to remove the top 1 cm of sediments from depositional areas in the streambeds. A scoop was used rather than the SOM as the sediment type was predominately coarse grained sand which prevents the shutter door on the sampler from sealing properly. Lake samples were collected using the 0-1 cm interval of sectioned cores. Both sieved ($60\mu\text{m}$) and unsieved

samples were collected. Sieved samples were collected to prevent bias introduced by differences in grain size from confounding results. Sieves were made from 60µm plastic mesh. The methyl to total mercury ratio was used as a proxy for methylation efficiency of the sediments; higher methyl mercury concentrations found in the sediments per unit of total mercury indicate higher methylation potential and bioavailability.

Wetland Sampling (Objective 4)

Investigation of the methylation efficiency of wetland versus non-wetland areas were conducted during May, 2001. Name, location, and a brief habitat description of the three wetland areas studied are listed in Table 3. At each area studied, sampling was conducted along a transect, one station furthest into the interior of the wetland (inner), one midway from the inner station to the outside of the wetland (middle), and one just outside of the wetland (outer). The Mandeville Island station had sediment containing peat, channels greater than two meters deep, and the water was well mixed and visually appeared to be equivalent to the adjacent San Joaquin River. Webber Point and Fourteen Mile Slough had silty sediment free of peat, limited water circulation, and were close to agricultural areas. At each station two replicate cores were collected, the sediment from each core was extruded and the sediment sub-sampled at the interval of 0-2 cm. The control sites were located on the San Joaquin River away from the wetlands and the sediments were silty and similar in appearance to Webber Point and Fourteen Mile Slough sediments. Samples were analyzed for total mercury, methyl mercury, and LOI.

Sediment Sampler

The upper portions of the sediment column are thought to be the most important in terms of trophic transfer and sediment/water flux. It is here that the sediment contacts the water, and the transition from oxic to anoxic usually occurs within a few millimeters in delta sediments (Gill, personal communication). The maximal rates of Hg methylation have been shown to occur just below the oxic/anoxic transition zone in sediments (Gilmour et al. 1992). In addition it is from this sedimentary layer that most diffusional flux originates (Gill et al. 1999), and it is here where most benthic infaunal invertebrates live. Therefore, a decision was made to sample the superficial 0-0.5 cm sediment interval

for the “survey” and “seasonal” work. This interval does not accurately characterize the total amount of mercury locked up in the sediment reservoir of the Bay-Delta, but does target the sediment stratum from which mercury is most likely to be mobilized into the water column. However, there are no commercially available samplers capable of reliably sampling this portion of the sediment column. A sampler was therefore designed and built to cleanly capture the top 0.5 centimeters of sediment. Picture 3 shows the SOM fully assembled with the trap door in the closed position and the trigger line attached ready for remote use. Picture 4 shows a close-up of SOM with the trap door open exposing the cleanly captured top 0.5 cm of sediment. Appendix A contains detailed instructions for the construction of the SOM sampler. The primary benefits of this sampler were the large sediment yield per deployment (~ 135 g), the straight forward sub-sampling of the targeted surface sediment interval, and the consistency in sampling the surface sediment interval. Unlike sectioning cores for a targeted sediment interval, where the sub-sampling is tedious and time consuming, this sampler required nothing more than scooping the sediment out of the sampler and into the sample container. The sampler is deployed remotely from a small boat by attaching a hand pole or line and weight depending on water column depth. In addition, the sampler may be used directly by a SCUBA diver.

Clean sample collection

Sediment samples were collected into 60 mL wide-mouth borosilicate glass jars, with Teflon™ lined polyethylene caps (I-CHEM™ EPA-clean, or equivalent acid-cleaned) using standard clean techniques. Clean techniques briefly described are as follows: sampling crews consisted of at least two persons, one wearing fresh clean room gloves “clean hands” and the other holding the sampler “dirty hands” (Picture 5). The clean hands person was responsible for transferring sediment from the sampler into the sample jar. The dirty hands person assisted while not coming into direct contact with the sample until the sample was contained. The jars were filled to 60-80 % of the container capacity with sediment (to minimize head-space losses of volatile Hg, while allowing for expansion due to freezing). The samples were kept on dry ice in the field and during transport back to the lab. Samples were frozen at < -10°C (ordinary freezer at lowest

setting) with a maximum holding time of 1 year. All homogenization and other handling of low-level samples (< 100 ng/g) were performed by clean-room gloved personnel in an area known to be low in atmospheric Hg. It should be noted that the clean techniques employed here were developed in conjunction with the MLML trace metals laboratories and Gary Gill of Texas A&M University at Galveston. These methods have been shown to be non-contaminating for mercury and methyl mercury at low environmental levels.

Laboratory Analysis

All mercury and methyl mercury analysis was performed using methods and quality assurance/quality control detailed in the CALFED Mercury Project QAPP (Puckett and van Buuren 2000, <http://loer.tamug.tamu.edu/calfed/>). Analysis of LOI was performed following standard method ASTM D2974. Grain size analysis was performed using standard methods of Plumb (1981).

RESULTS AND DISCUSSION

Quality Assurance/Quality Control

MLML participated in three intercomparison studies and sent splits of sediment samples to Frontier for total and methyl mercury analysis. All QA results are listed in Appendix C of this report. Results of the intercomparison studies can be obtained at the CALFED Mercury Project website (<http://loer.tamug.tamu.edu/calfed/DraftReports.htm>). The results of the first intercomparison study showed good interlaboratory precision for total mercury in sediment. Results for methyl mercury in sediment showed a larger degree of variability possibly due to a slight low bias by one of the participating laboratories (van Buuren, 2003). The third intercomparison study showed good interlaboratory precision for both total and methyl mercury in sediments (van Buuren, 2002). The relative percent differences (RPDs) between split sediment samples analyzed for total mercury at MLML and Frontier ranged from 1 – 20 percent, while the RPDs for split sediment samples analyzed for methyl mercury ranged from 10 – 172 percent. The total mercury split data shows good interlaboratory precision. The high RPDs of samples

analyzed for methyl mercury may be attributed to the difficulties associated with splitting a heterogeneous natural sediment sample containing decomposing vegetation and woody debris (a common characteristic of delta sediments) rather than a potential analytical problem. It should be noted that six sieved samples were split and analyzed for methyl mercury by both MLML and Battelle Laboratories resulting in RPDs ranging from 0.8 – 56.1 percent. The lower RPDs for sieved samples than unsieved samples points toward the splitting of heterogeneous sediment samples as a potential problem which may confound results of split samples far more than any analytical variation between laboratories. In addition, Bloom (2003), found thawed sediment samples kept refrigerated resulted in an increase in methyl mercury concentration when compared to samples kept frozen prior to analysis. Further investigations should be made to set up protocols for split samples to minimize variation from sample handling protocols. For future sediment split intercomparison studies, strict protocols should be followed to insure the samples are split in the field and kept frozen until analyzed. At no time should intercomparison samples be thawed and analyzed at one laboratory with an aliquot refrozen and transported to a second laboratory for analysis. Currently it remains unclear if the observed differences in methyl mercury concentrations measured at participating laboratories are attributable to analytical procedures, splitting methodology, or natural variation.

Small Scale Variation

An estimate of the small scale variation in sediment concentrations of methyl mercury and total mercury at locations sampled in the Bay-Delta is listed in Tables 4 & 5. The relative percent difference (RPD) of duplicate methyl mercury samples collected during the initial survey ranged from 19 to 108 percent (Table 4), while RPD's for total mercury were 4 to 82 percent (Table 5).

Figure 7 shows the small scale variation of methyl mercury in sediments collected from the west and east side of the river channel at East Columbia Cut in the central delta. The small scale variation between replicates collected from the west side of the channel was less than that of samples collected from the east side of the channel. The sediment of the west side was fine grained and homogenous with no submerged aquatic vegetation

visible in the sample (Picture 4) while the sediment of the east side was a heterogeneous mix of sand and silt covered with both submerged and floating aquatic vegetation (Picture 6). These results emphasize that small scale variation in methyl mercury concentration is expected to increase in locations within the Bay-Delta with heterogeneous sediment types having an abundance of submerged aquatic vegetation present.

Geographical Trends

San Pablo Bay and South Bay sediment total mercury concentrations were typically found to be around 0.3 ppm (Figure 2). The total mercury concentrations in sediments around the Oakland inner harbor were approximately 1 ppm with Brooklyn harbor (Station # 283) being ten times higher at 9.4 ppm (Figure 2). Methyl mercury sediment concentrations in San Pablo Bay were less than 1 ppb (Figure 3). A few locations in the middle South Bay around Oakland Harbor had methyl mercury concentrations above 2 ppb (Figure 3). The highest methyl mercury concentration found in the South Bay was 15.89 ppb at Coyote Hill Slough (Station # 310) (Figure 3). There was no correlation between methyl mercury and LOI. The amount of methyl mercury to the total mercury present in sediments of San Pablo Bay and South Bay was approximately one half to one percent (Figure 4). Two locations, Richmond Inner Harbor (Station # 273) and Coyote Hill Slough (Station # 310) had percent methyl mercury values of three and eight respectively (Figure 4). The methyl mercury concentrations in Oakland harbor appear to be a result of higher total mercury concentrations and not the result of a favorable habitat for mercury methylation as indicated by the ratio of methyl mercury to total mercury being consistent with surrounding locations sampled. In contrast, the high methyl mercury sediment concentrations in the Richmond Inner Harbor (Station # 273) and Coyote Hill Slough (Station # 310) are likely due to favorable conditions for mercury methylation and methylation is occurring independent of the total amount of mercury present in the sediment.

Total mercury in the Bay-Delta decreased moving north to south from the northern tributaries of Prospect Slough and Cosumnes River into the central and southern

Delta (Figure 8). Total mercury concentrations of sediments in the northern tributaries were as high as 0.4-0.5 ppm in contrast to the central Delta with mercury concentrations from 0.1-0.3 ppm. The southern Delta sediments typically had very low mercury concentration; the greatest cluster of samples below the method detection limit (MDL) were found in the southern portion of the Delta. These results are consistent with the findings of Slotten et al. (2003).

A second spatial trend observed was an increase in total mercury (0.15 to 0.30 ppm) moving east to west from the central Delta into Suisun Bay and Grizzly Bay (Figures 8). Total mercury concentration increased with an increase in longitude when constrained by 38.00-38.15 degrees latitude (Figure 9). The Carquinez Strait, Suisun Bay, and Grizzly Bay areas had a large number of sites with high total mercury concentrations. Generally, sediments in the San Pablo and Suisun Bays averaged 0.3 ppm with some sites above 0.5 ppm total mercury. It is possible for sediment concentrations to be biased by changes in grain size. In this case, however, the increase in total mercury concentration moving out of the Delta was not a bias introduced by a change in grain size as the normalized and un-normalized total mercury concentration versus longitude yield similar correlation coefficients (normalized to percent fines data not shown).

In contrast to the geographic patterns of total mercury, methyl mercury generally increased from north to south moving into the central Delta from the northern tributaries (Prospect Slough and Cosumnes River) (Figure 10). The central Delta consistently had higher methyl mercury concentrations than the perimeter waterways and adjacent bays. Methyl mercury concentrations were very low or non-detectable (MDL= 0.019 ppb) in the Sacramento River and San Joaquin River channels moving west, out of the central Delta. At the convergence of the Sacramento and San Joaquin Rivers (Sherman Island area) methyl mercury concentrations increased to values as high as many of the central Delta sites (Figure 10). Joyce Island in Grizzly Bay had the highest methyl mercury sediment concentration (9.3 ppb) of all sites sampled in the North Bay and Delta.

The ratio of methyl mercury to total mercury was used to identify locations within the Bay-Delta with high mercury methylation potential (Figure 11). The central Delta had the greatest potential for mercury methylation; many sites in the central Delta had

greater than 2 % of the total mercury as methyl mercury. Franks Tract had the largest measured ratio (2.6 %). In addition, other sites within the central Delta appeared to have large methylation potentials as total mercury concentrations were below the MDL and a considerable amount of methyl mercury was present (Figure 11- grey scale bars). However, the ratios at these sites were estimated using the MDL value of 10.5 ppb as a value for total mercury and, therefore, must be considered only as estimated potentials. All of the tributaries surrounding the central Delta (e.g. Prospect Slough, Cosumnes River, Sherman Island, the upper San Joaquin River, and southern Delta) had very low mercury methylation potentials. Although Honker Bay had many sites with relatively high methyl mercury concentrations only one site (Joyce Island) showed a large potential for mercury methylation (2.3 % methyl mercury). A comparison of the methylation potential of the central Delta and the surrounding tributaries indicates the central Delta possesses environmental conditions favorable for mercury methylation. An understanding of the factor/s forming these optimal conditions is desirable to control the production of methyl mercury in the Bay-Delta sediments.

Numerous field-based studies have suggested that organic carbon is positively correlated with methyl mercury in sediments (Choi and Bartha 1994, Hurley et al. 1998, Krabbenhoft et al. 1999). In addition, lab based studies have shown that organic carbon is positively correlated to methyl mercury production (Olson and Cooper 1976, Furutani and Rudd 1980, Wright and Hamilton 1982, Lee and Hultberg 1990). Consistent with these studies, LOI (a proxy for total organic carbon) was significantly correlated ($R^2 = 0.32$) to methyl mercury concentration in Delta sediments (Figures 12). However, the low correlation coefficient indicates other factors, in addition to LOI, likely control methyl mercury production in Delta sediments.

Regnell et al. (1997) indicated that total mercury correlated positively with methyl mercury in surficial sediments of a seasonally stratified lake in southern Sweden. One of the reactants in the mercury methylation reaction is Hg^{2+} therefore the concentration of Hg^{2+} in a system might be expected to have an effect on the rate of formation, and the concentration, of methyl mercury (Kelly et al. 1995). Rudd et al. (1983) reported a linear relationship between amount of Hg^{2+} added to lake sediments and rate of formation of methyl mercury, demonstrating that in a system where all else remained constant,

methylation was first order with mercury concentration. In this study, a weak positive correlation was found between methyl mercury and total mercury concentrations in sediments (Pearson's $r^2 = 0.19$, $n = 99$, $p < 0.01$) (Figure 13). The correlation between methyl mercury and total mercury indicates total mercury may play a role in the production of methyl mercury, however, the correlation is weak and is dependent on throwing out 4 % of the data as outliers.

In a study of the Florida Everglades, factors such as wetland density, low surface water pH, and sulfide were shown to be important in controlling methyl mercury production (Gilmour et al. 1998). Factors other than total mercury and organic carbon may have a much stronger influence on the production of methyl mercury in the Bay-Delta. Strategies to control methyl mercury production in the Bay-Delta should consider the relative importance of total mercury, organic carbon, as well as the many factors mentioned above. Currently, the relative contribution to which each of these factors influences methyl mercury production in the Bay-Delta is unknown.

Trends across Habitat Types

All samples collected within the delta during the initial survey fell into habitat types defined by wetland inventories GIS maps. The methyl mercury concentrations for all of the samples assigned to a particular habitat type were averaged to give an average methyl mercury concentration and error for each habitat type. Table 1 lists the methyl mercury sediment concentrations of each habitat sampled in the delta during the initial survey. The marsh habitats had methyl mercury concentrations above 1 ppb. Lakes and ponds also had concentrations above 1 ppb, however, it must be pointed out that only two samples were collected from this habitat type. Farmed wetlands, seasonal wetlands, open water, and mudflats had methyl mercury concentrations less than 1 ppb. A large number of open water samples were collected and as a result there is high confidence that this habitat type is accurately characterized. Ideally all habitat types should be sampled as thoroughly as the open water habitats were. The riparian woodland and upland habitats had methyl mercury sediment concentrations less than 0.25 ppb. This work identifies the marsh habitat type as a potential source of methyl mercury as the average methyl mercury concentrations are higher than all other habitat types sampled. In addition, the farmed

wetlands could be an important source of methyl mercury as the percent coverage of this habitat type is large with respect to the total area of the delta and the methyl mercury concentrations are relatively high compared to other habitat types.

Seasonal Trends

Solid phase methyl mercury showed distinct seasonal patterns at locations within the central Delta and Cosumnes River (Figure 14, panels c-f). Methyl mercury concentrations at Franks Tract, Connection Slough, and Cosumnes River were elevated twice per year (Figure 14, panels c, d, f). The largest peak occurred during summer and the smaller peak occurred over winter. The winter peak, although lesser in magnitude (approx. 2 ppb), was generally a longer lasting feature (3-4 months) while the summer peak reached a maximum (approx. 6 ppb) and decreased within 1-2 months. Methyl mercury in the sediments at Prospect Slough remained constant (approx. 1 ppb) over the length of the study (Figure 14, panel a). Sherman Island had an extended period of elevated solid phase methyl mercury concentration summer and fall of 2000, followed by a decrease in concentration throughout the remainder of the study (Figure 14, panel b).

Connection Slough was the only site sampled where a repeating summer methyl mercury peak was observed. No summer peak was found at Franks Tract or White Slough during the summer of 2000 (Figure 14, panels c, e), perhaps as a result of the sampling frequency. The sampling frequency was once per month at Franks Tract and White Slough during the summer of 2000, and it is probable that this interval allowed the summer peaks to go undetected. The 2001 summer peak at Franks Tract occurred very rapidly, and sampling twice per month was necessary to capture the event. Gill et al. (1999) also reported a rapid seasonal increase and decrease of methyl mercury, which necessitated frequent sampling during a study done in Lavaca Bay, Texas.

Total mercury sediment concentrations showed no seasonal trends (Figure 14, panels a-f). However, at Sherman Island, total mercury concentrations were higher during the first half of the study and generally decreased throughout the second half of the study; a similar trend was found for methyl mercury (Figure 14, panel b). Total mercury concentrations demonstrated increased variability at Prospect Slough and Sherman Island, as compared with the central Delta and Cosumnes River. The largely

variable concentrations at Prospect Slough and Sherman Island may be the result of bias due to mean grain size, as high water flow and a scoured bottom characterize these locations. Within the central Delta, White Slough had the least variable total mercury concentrations, and Cosumnes River consistently had the highest total mercury concentrations (Figure 14, panel e, f).

Bloom et al. (1999) used the methyl mercury to total mercury ratio in sediments to evaluate the seasonal variation of mercury methylation. Gilmour et al. (1998) found *in situ* production of methyl mercury controlled concentration in the Florida Everglades. The seasonal changes in sediment methyl mercury concentration observed in the Bay-Delta were likely the result of increased *in situ* production resulting from a stimulation of the microbial activity within the within the sampled stratum. Evidence of *in situ* production is found in the methyl mercury to total mercury ratio being driven by changes in methyl mercury meaning the methyl mercury concentrations were increasing as the total amount of mercury remained unchanged. Pore water concentration gradients determined by Gill (2003) also support *in situ* production as the source of methyl mercury as the methyl mercury concentrations in pore waters were always higher than the overlying water concentrations. Conversely, the spring and summer peak in methyl mercury may have resulted from movement of the peak methylating layer into and out of the sampled sediment interval and not from increased *in situ* methylation within the sampled stratum. This could occur because the peak microbial production of methyl mercury occurs in a thin zone near the oxic/anoxic interface in the vertical sediment profile (Gilmour et al. 1992) and the oxic/anoxic boundary can be expected to shoal in sediments during periods of low flow and high temperatures. However, dissolved oxygen profiles determined on intact cores using microelectrodes indicate that the oxic/anoxic interface remains in the top 0-1 cm interval in delta sediments (Gill, 2003). Furthermore, solid phase methyl mercury vertical profiles in sediment cores collected from the delta during this study do not support a vertical movement of methyl mercury with season that would explain the observed temporal shifts in surficial methyl mercury concentrations (Gill, 2003).

Sulfate reducing bacteria are especially important methylators of mercury (Gilmour et al. 1992). Factors that increase sulfate reduction rates, such as high water

temperature, high availability of organic carbon, and high sulfate concentrations are likely to increase the production of methyl mercury (Compeau and Bartha 1985, Gilmour et al. 1992). Water temperature in the Delta fluctuates annually following a sinusoidal curve with maximum summer water temperatures of approximately 20 °C and winter minimum temperatures of approximately 10 °C. Consistent with the findings of Gilmour et al. (1998) in a study of the Florida Everglades, methyl mercury sediment concentrations in the Bay-Delta were elevated during periods of warm water temperatures. In contrast to the positive correlation between LOI and methyl mercury described in Objective 1c the seasonal increase in methyl mercury concentration occurred independent of changes in LOI (data not shown). A possible explanation is the inability of the LOI determinations to make any statement to the quality of the carbon present. Stimulation of microbial activity and any resultant production of methyl mercury is dependent in part on the availability of labile carbon; LOI is a description of the total amount of carbon, both labile and refractory. Sediments containing a large fraction of refractory material such as peat would give a high value for LOI with little benefit to the microbial community.

There was no relationship between total mercury and methyl mercury concentrations at the seasonal study sites which exhibited a summer increase in methyl mercury production (Figure 15). The highest methyl mercury concentrations occurred over a broad range of total mercury concentrations. In contrast to the overall picture, however, if only the Sherman Island site is considered, there was a positive linear relationship between methyl mercury and total mercury ($R^2 = 0.40$) (Figure 15). A predictive model of methyl mercury based on total mercury concentrations determined from the Sherman Island data would not be useful on a basin wide scale as changes in environmental conditions negated the first order relationship between total mercury and methyl mercury.

Determining the primary factors responsible for the seasonal increase in production of methyl mercury was beyond the scope of this study, although it is likely that temperature plays a role, as does available organic carbon. The use of total mercury concentration as a predictor of methyl mercury production was useful only in locations where seasonal changes in environmental conditions were minimal. Further research is

needed to understand the processes and combination of environmental factors that promote mercury methylation during spring and summer in the Bay-Delta.

Mercury Bioavailability

During the California gold rush era, mercury was mined in the coastal mountains and transported to the Sierra Mountain Range for use in Gold mining. Mercury mined from the coastal range was in the form of cinnabar while the Sierra Range was contaminated exclusively with refined mercury (elemental). These forms of mercury have very different behaviors in terms of reactivity and solubility. One important question to ask is *are* the mercury species found in these mountain ranges equally available for mercury methylation (bioavailable). Finding dissimilar methyl mercury to total mercury ratios in the coastal and Sierra range watersheds would be evidence that mercury in the coastal and Sierra ranges are not equally available for methylation.

The comparisons of coastal versus Sierra range total mercury concentrations, methyl mercury concentrations, and the methyl mercury to total mercury ratios for unsieved sediment samples are shown in Figure 16. Coastal and Sierra range lakes had equivalent levels of total mercury, methyl mercury, and methyl mercury to total mercury ratios. Total mercury concentrations were much higher (18,000 ppb) in coastal mountain streams, near mine sites, than Sierra mountain streams (49 ppb) and slightly higher in coastal valley streams (122 ppb) than Sierra valley streams (33 ppb). Methyl mercury concentrations were equivalent in coastal and Sierra mountain and valley streams. The methyl mercury to total mercury ratios in Sierra mountain and valley streams were significantly higher than coastal mountain streams. However, it is important to point out the large standard error associated with the Sierra valley stream data.

In an attempt to reduce any bias introduced by grain size variability and determine the methylation potential of only the fine-grained fraction, samples were sieved through a 60µm screen. Figure 17 shows the comparisons between coastal and Sierra range total mercury concentrations, methyl mercury concentrations, and the methyl mercury to total mercury ratios for sieved sediment samples. Trends in total mercury and methyl mercury of sieved samples are similar to unsieved samples (Figures 16 & 17). Both coastal and Sierra range lakes had equivalent total mercury, methyl mercury, and methyl mercury to

total mercury ratios (Figure 17). Total mercury concentrations were higher in coastal mountain and valley streams than Sierra mountain and valley streams while methyl mercury concentrations were equivalent. The methyl mercury to total mercury ratio in Sierra mountain streams was significantly higher than coastal mountain streams but, unlike the unsieved results no difference was found in the methyl mercury to total mercury ratios of coastal and Sierra valley streams.

The permanent lakes were significantly lower (Least Significant Difference multiple comparison test, $p < 0.05$) in methyl mercury concentration and the methyl mercury to total mercury ratio than valley or mountain streams (Figures 17). This is in contrast to the seasonal lakes (Capay Dam and Cache Creek Settling Basin), in which some of the highest concentrations of methyl mercury occurred (8 and 4 ng/g dry weight sediment respectively). These results are consistent with other studies showing newly flooded wetlands and reservoirs experience an increase in methyl mercury production (Bodaly et al. 1993, Kelly et al. 1995, Kelly et al. 1997). Kelly et al. (1997) concluded that the large increases in methyl mercury concentrations were a result of increased net production of methyl mercury rather than release of methyl mercury that was in the wetland prior to flooding. The increase in methyl mercury, at these newly flooded areas, is likely linked to increased microbial activity in response to a change in environmental conditions. Three changes in environmental conditions known to stimulate methylation of mercury are 1) sudden death of vegetation supplying a large amount of organic carbon to become available for decomposition, 2) high decomposition leading to an increase in anaerobic habitat, and 3) mercury methylation stimulated by increased temperature (Kelly et al. 1997). Capay Dam and the Cache Creek Settling Basin experience all three of these changes in environmental conditions on an annual basis allowing an increase in methyl mercury production to occur independent of an increase in total mercury.

The most significant finding of the mercury bioavailability study was the higher methylation potentials (greater bioavailability) of sediments from the Sierra mountain streams compared to coastal mountain streams. This is perhaps a problem of definition because the total mercury concentrations near the mine site stations in the coast Range are relatively high, greater than 10,000 ppb, which drives the low methyl mercury to total mercury ratios. However, the methyl mercury concentrations in the two watersheds were

equivalent, indicating that the large pool of mercury in the coastal range was largely unavailable for methylation.

Current work suggests mercury in the upper watershed of the coastal range is significantly less available for methylation than the mercury in the Sierra range. However, as coastal range mercury is transported through the watershed into the Bay-Delta it becomes more available for methylation. Other work supporting this working hypothesis is that the sediment, clams, and fish collected at the mouths of the tributaries coming from both ranges have equivalent total and methyl mercury concentrations (Davis et al., 2003; Slotten et al., 2003; Foe et al., 2003).

Mercury at the mine sites is likely to start out as cinnabar and, through diagenic processes in the sediment, becomes more bioavailable for methylation. Paquette and Heltz (1995) showed that high concentrations of sulfide leading to the formation of soluble polysulfide complexes increase the solubility of cinnabar. In addition, it has been demonstrated that organic rich sediments are capable of enhancing the dissolution of cinnabar (Ravichandran et al. 1998, Wallschlager et al. 1998). The Cache Creek watershed has high levels of sulfide as a result of thermal springs (Domalgalski, 2003), which could enhance cinnabar dissolution. The average LOI for Cache Creek is 6 percent making it unlikely that organic matter is responsible for the cinnabar dissolution. Clearly, additional studies directed towards further testing of this working hypothesis are needed. One question left unanswered is *what* role if any does differing environmental conditions play in the methylation efficiency of coastal versus Sierra range derived mercury.

Wetland Study

The investigation of wetlands to determine if methylation potentials were higher in the interior than adjacent waterways showed clear patterns in both methyl mercury concentrations and the methyl mercury to total mercury ratios (Figure 18 & 19). Methyl mercury concentrations at the interior of all wetland areas studied were higher than concentrations at the exterior of the wetlands (Figure 18). In addition, the methyl mercury to total mercury ratio was highest at the interior of all three wetlands studied

(Figure 19). LOI was significantly correlated to both methyl mercury ($p < 0.001$) and the methyl mercury to total mercury ratio ($p < 0.001$) (Data not shown).

Numerous studies have shown wetland areas to be areas of high methyl mercury production (St. Louis et al. 1994, Hurley et al. 1995, Rudd 1995, St. Louis et al. 1995, Krabbenhoft et al. 1999). The common features of these areas are limited circulation, proximity to agricultural areas, and lack of peat in the sediments. The LOI levels in the sediment in the interior of these wetlands appeared to be high (7-50%) relative to those in the main, well flushed, part of the Delta (usually $< 5\%$). Water circulation in the interior of the wetland areas was limited and led to increased water temperature and residence time. The large amount of organic material present and the limited circulation of the water likely led to hypoxic water conditions. The combination of these environmental conditions set the ideal stage for mercury methylation in the presence of reactive mercury (Kelly et al. 1997). Clearly the wetland areas within the Bay-Delta have a high potential for production of methyl mercury. Further research is needed to quantify the production of methyl mercury in the wetland habitats and determine the contribution these habitats make with respect to the mercury budget of the entire Bay-Delta.

CONCLUSIONS

In brief summary, the major findings of the study are listed below.

- The highest methyl mercury sediment concentrations were found in the central Delta. The central Delta had the greatest mercury methylation potential when compared to the surrounding tributaries.
- Solid phase methyl mercury concentrations varied seasonally with highest concentrations occurring during late spring/summer.
- Coastal mountain streams had two orders of magnitude higher total mercury concentrations than Sierra mountain streams and the methyl mercury concentrations were equivalent.
- Interiors of wetlands consistently had higher solid phase methyl mercury concentrations and methyl mercury to total mercury ratios than fringes of wetlands.

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Table 1. A list of habitat types defined for the delta with the corresponding area, number of samples collected, and MMHg concentration.

Habitat Type	Area Km²	Number of samples	[MMHg] (ng g⁻¹)
Upland	3751	2	.19 ± .03
Riparian Woodland	41	4	.24 ± .08
Mudflats	3	2	.50 ± .32
Open Water	238	36	.54 ± .06
Seasonal Wetlands	167	3	.55 ± .06
Farmed Wetlands	1447	8	.71 ± .20
Lakes and Ponds	35	2	1.26 ± .43
Marsh	51	7	1.46 ± .35
Total	5733		

Table 2. Name, location, and habitat type of seasonal monitoring sites

Name	Latitude	Longitude	Habitat Classification
Prospect Slough	38.28961	121.66239	Open water / fringe wetland
Sherman Island	38.04120	121.81930	Tidal wetland / riparian marshland
Franks Tract	38.05250	121.59191	Open water
Connection S	38.01250	121.55002	Channeled waterway /fringe wetland
Cosumnes River	38.25823	121.42618	Riparian marshland
White Slough	38.08723	121.47837	Fringe tule

Table 3. Name, location, and habitat type of wetland sampling sites			
Name	Latitude	Longitude	Habitat Classification
Mandeville Cut	38.06152	121.53774	Peaty sediment, Tule wetland
Fourteen Mile Slough	38.00659	121.39224	Silty sediment, Wetland, backwater
Webber Point	38.00965	121.44651	Silty sediment, Wetland, backwater
Control	38.00397	121.44416	San Joaquin River Channel

Table 4. Relative percent difference(RPD) between field replicates for sediment samples collected October 1999 and analyzed for methyl mercury.

Station Number	Station Name	Rep 1 (ng/g)	Rep 2 (ng/g)	RPD
47	Sacramento River	0.18	0.30	50.3
54	Snodgrass River	0.26	0.08	108.3
91	SJR Jersey Pt.	0.04	0.06	48.8
95	San Joaquin River	<MDL	<MDL	
104	Kimball Island	0.40	0.49	20.7
105	San Joaquin River	0.44	0.21	67.8
175	SJR @ Landers Ave	0.04	0.03	28.7
203	Port of Stockton	0.32	0.40	22.1
213	Liberty island	0.47	0.25	62.5
357	Cosumnes at Wilton	0.10	0.13	19.3
359	Cosumnes River	0.04	0.05	26.7
990	Cache Creek	0.13	0.21	48.7
991	Capay Dam	5.87	2.20	91.0

Table 4. Relative percent difference (RPD) between field replicates for sediment samples collected October 1999 and analyzed for total mercury.

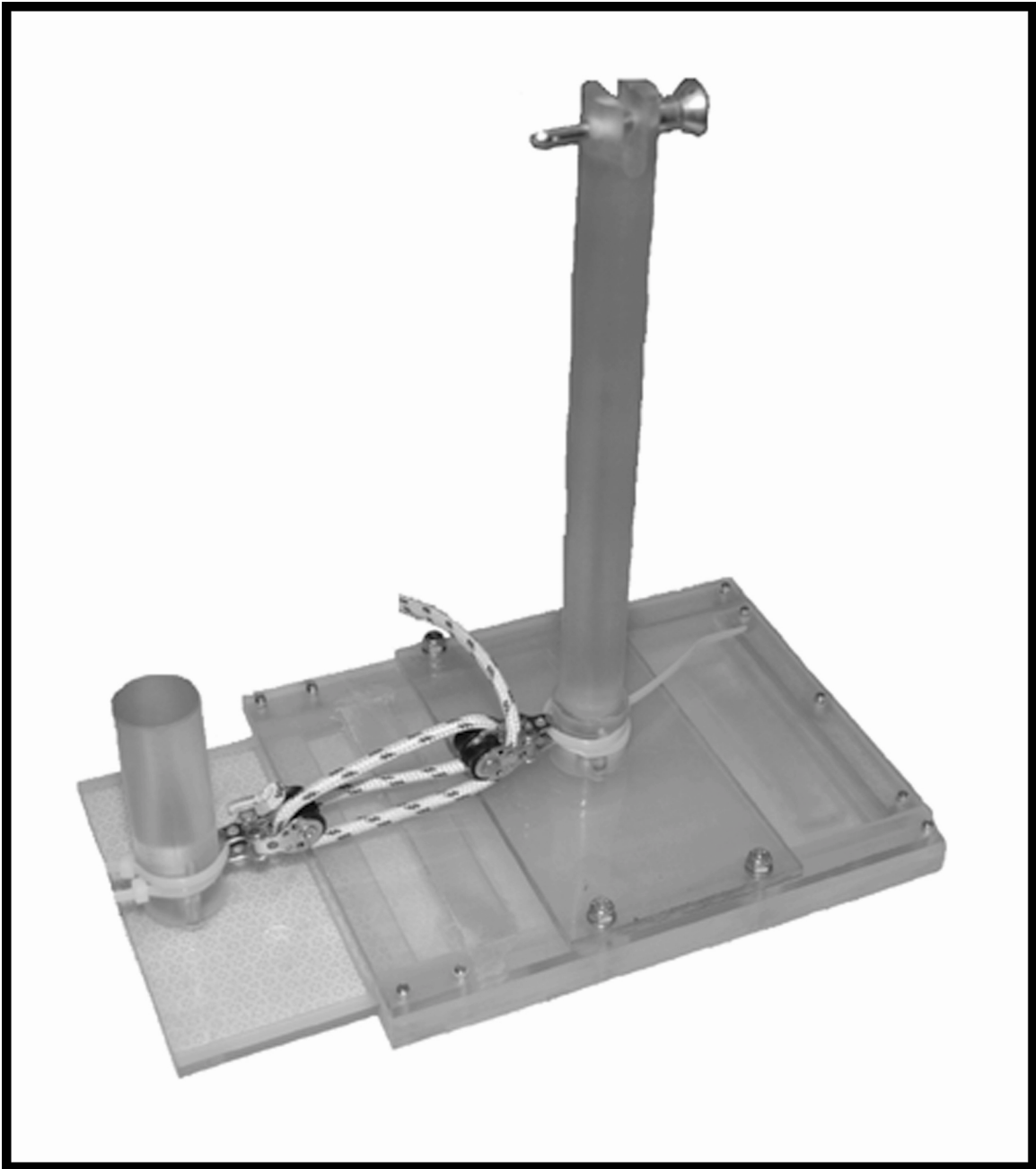
Station Number	Station Name	Rep 1 (ng/g)	Rep 2 (ng/g)	RPD
36	Cache Slough	130.7	125.3	4.2
47	Sacramento River	61.1	32.6	60.7
50	Georgina Slough	81.1	85.1	4.8
54	Snodgrass River	46.1	27.6	50.3
64	Beaver Slough	190.1	160.3	17.0
67	Tower Park	135.7	156.3	14.1
71	Little Connection S	82.5	35.1	80.7
82	Connection Slough	110.9	125.8	12.6
85	Frank's Tract	78.5	68.2	14.0
88	Fisherman's Slough	156.8	206.9	27.5
91	SJR Jersey Pt.	33.1	79.9	82.9
93	Big Break	151.5	175.6	14.7
95	San Joaquin River	29.2	26.6	9.4
103	Antioch Dunes	57.6	100.4	54.2
104	Kimball Island	235.7	192.1	20.4
105	San Joaquin River	250.9	228.5	9.3
123	Suisun Bay Marsh	178.1	250.5	33.8
175	SJR @ Landers	<MDL	<MDL	
203	Port of Stockton	193.8	181.1	6.8
215	Liberty Cut Marsh	312.6	220.3	34.6
357	Cosumnes at Wilton	<MDL	<MDL	
359	Cosumnes River	<MDL	<MDL	
990	Cache Creek	93.0	86.6	7.1



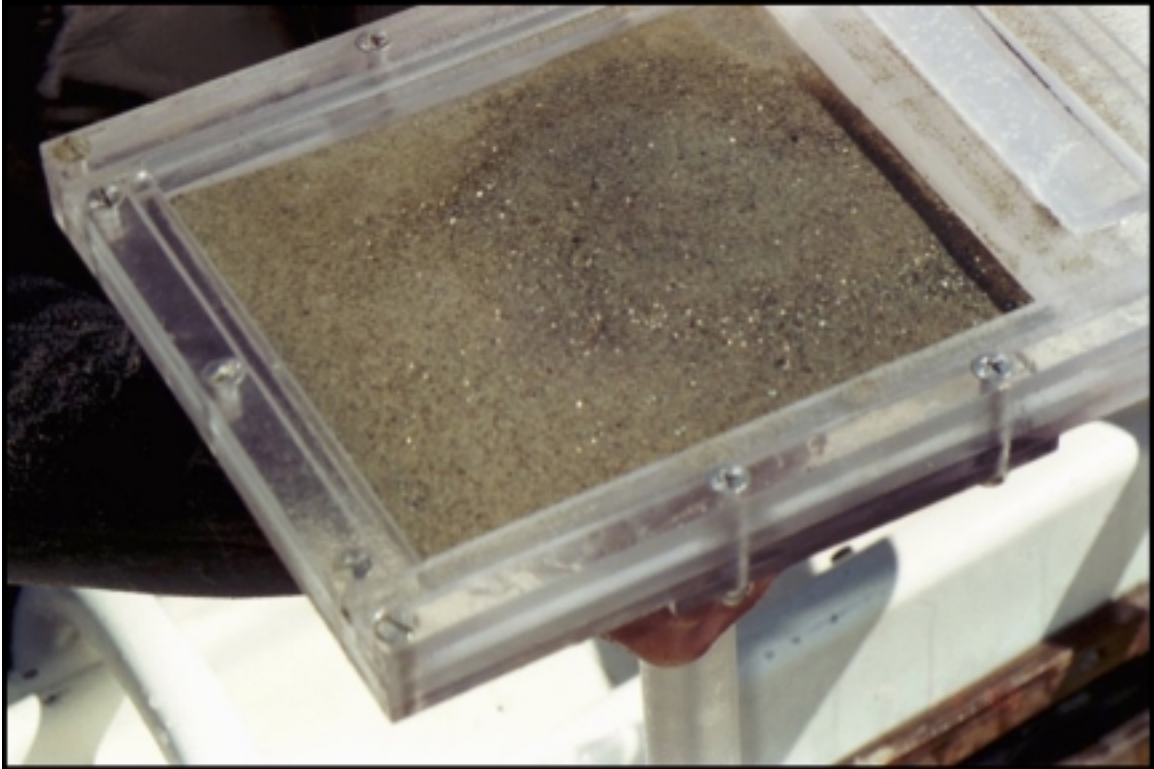
Picture 1. A picture showing the fringe marsh habitat along rip-rap waterways at Mandeville Island located near Franks Tract in the central Bay-Delta. (Photo by W. Heim)



Picture 2. This picture of Tower Park marina in the Bay-Delta illustrates the subsidence of croplands and the necessity of levees for prevention of flooding. (Photo by W. Heim)



Picture 3. An assembled Sludge O Matic with attached shutter trigger line. The door is shown in the closed position. The attachment of the pulley system with plastic ties is clearly shown as is the handle configurations and aircraft pin. (Photo by W. Heim)



Picture 4. Close-up photo of the topmost 0.5 cm of sediment captured cleanly using the SOM. The trap door of the sampler is shown in the open position with sediment ready to be transferred into sample jars. (Photo by W. Heim)



Picture 5. Field team employing “clean hand techniques” at Sherman Island. Sediment is being sub-sampled from the SOM using a plastic scoop to transfer samples. “Clean hands” person is wearing clean room gloves during all sub-sampling. “Dirty hands” person never comes into contact with the sample but aids “clean hands” person as necessary. (Photo by R. Lehman)



Picture 6. Shallow water environment of East Columbia Cut characterized by a mixed sediment type of sand and silt with an abundance of floating and submerged aquatic vegetation.

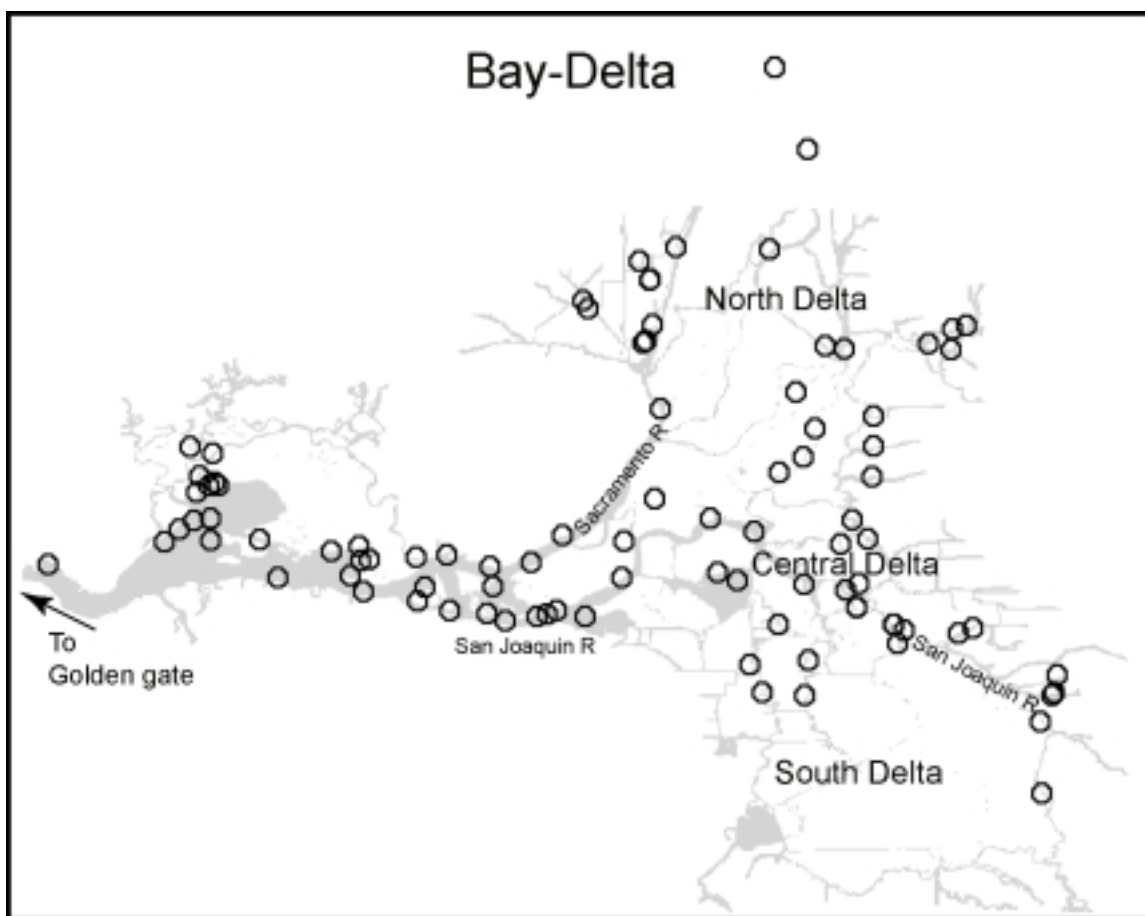


Figure 1. Map showing the spatial survey sampling locations (○) within the delta and Grizzly Bay.

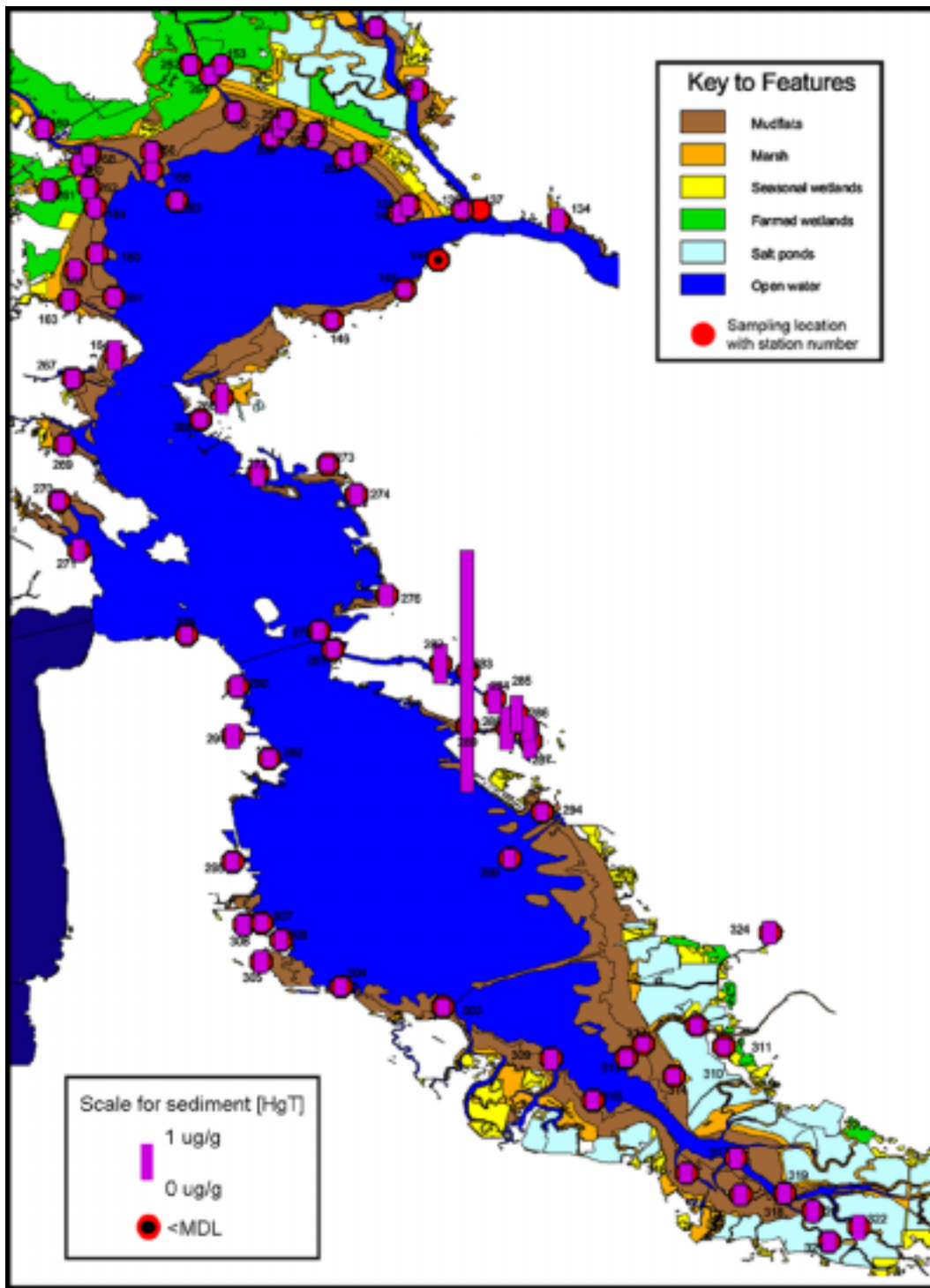


Figure 2. Total mercury surficial (0-0.5 cm) sediment concentrations of San Francisco Bay are indicated by purple scale bars with the key given in the lower left. The Key to Features shown in the upper right gives a color code for different habitat types found in the Bay as described by the National Wetlands Inventory. Sampling locations are represented as red circles.

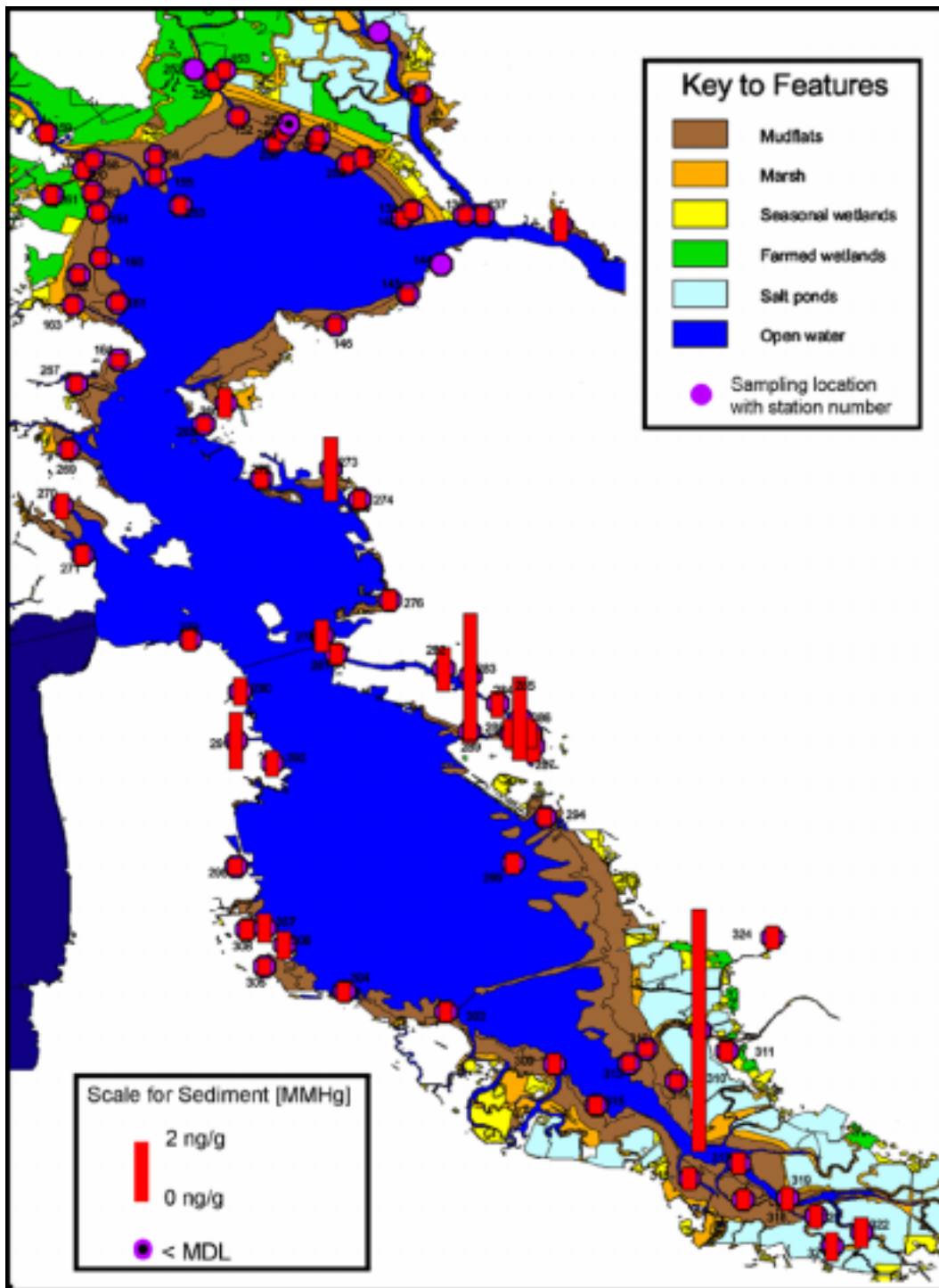


Figure 3. Methyl mercury surficial (0-0.5 cm) sediment concentrations of San Francisco Bay are indicated by red scale bars with the key given in the lower left. The Key to Features shown in the upper right gives a color code for different habitat types found in the Bay as described by the National Wetlands Inventory. Sampling locations are represented as purple circles.

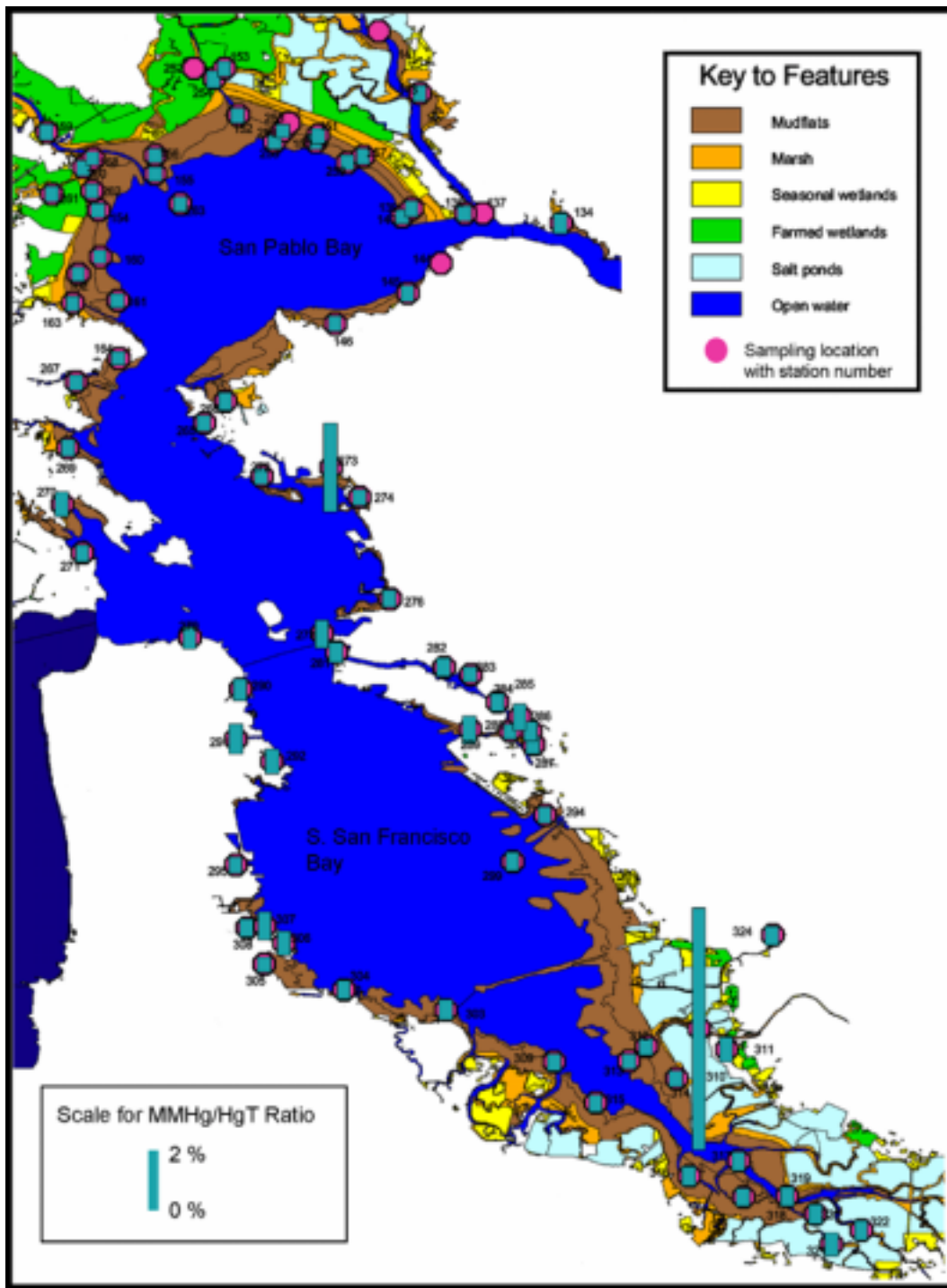


Figure 4. Methyl mercury to total mercury ratios (as a percent) in surficial (0-0.5 cm) sediment of San Francisco Bay are indicated by aqua scale bars with the key given in the lower left. The Key to Features shown in the upper right gives a color code for different habitat types found in the Bay as described by the National Wetlands Inventory. Sampling locations are represented as pink circles.

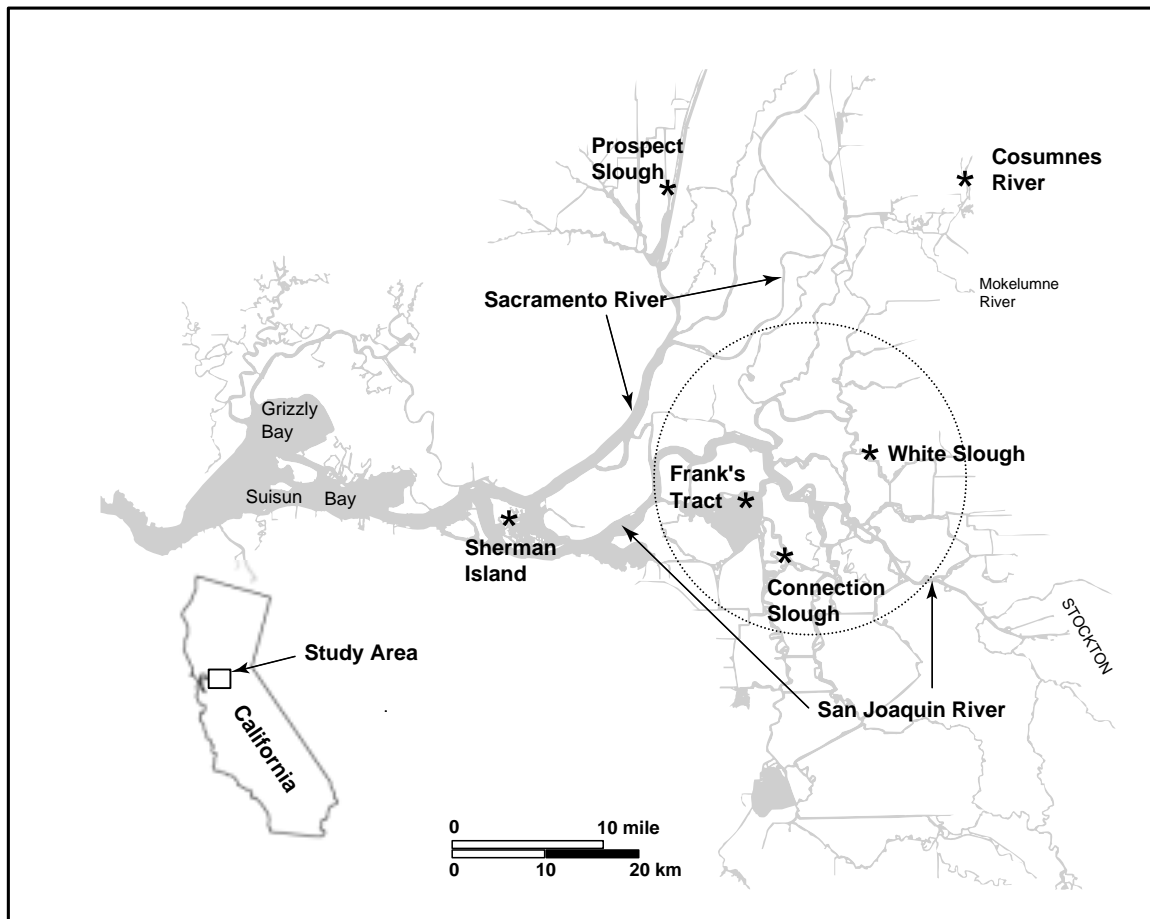


Figure 5. A map of the San Francisco Bay-Delta showing the surrounding tributaries and Bays. The six seasonal sampling stations are shown with asterisks and the following names: Prospect Slough, Cosumnes River, White Slough, Franks Tract, Connection Slough, and Sherman Island. The dashed line circle represents the approximate boundary of an area within the study area operationally defined as the “central delta”.

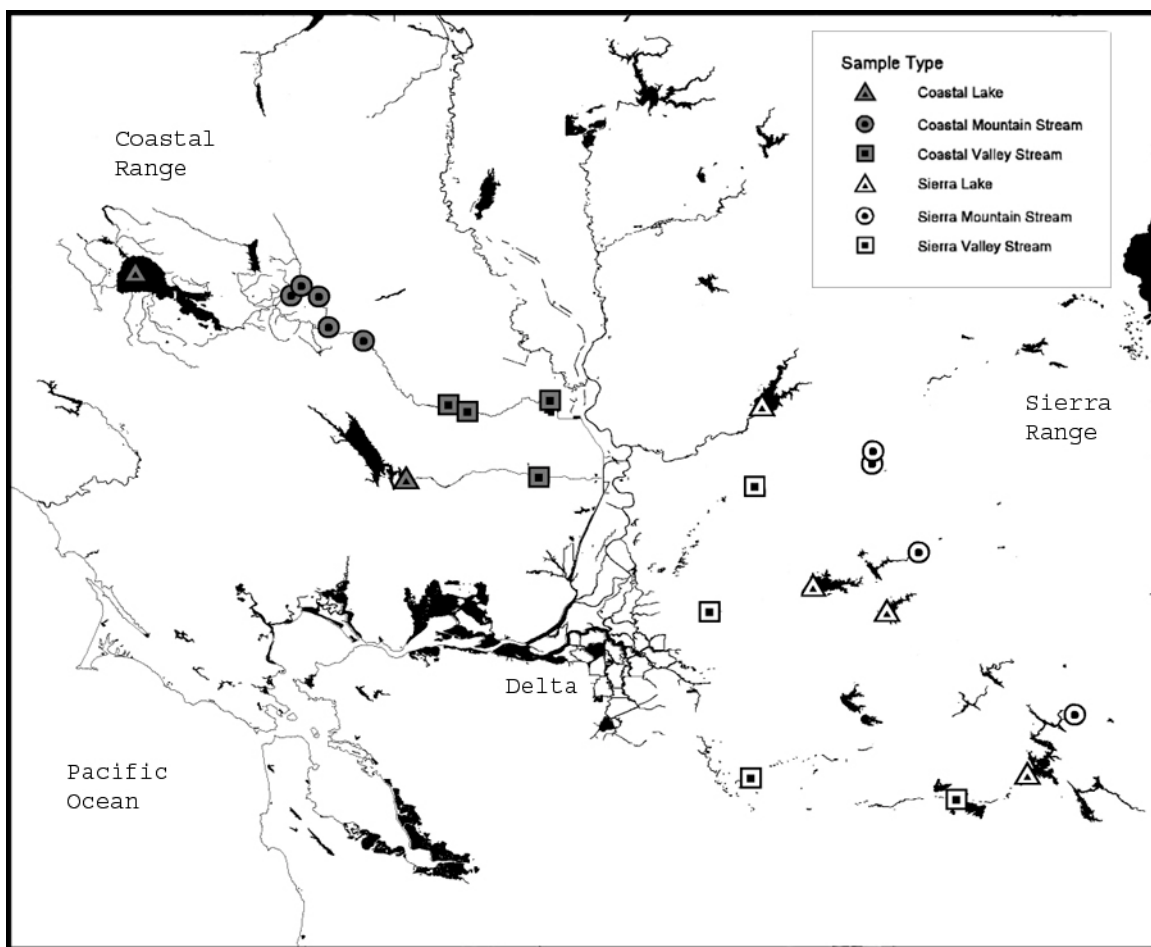


Figure 6. Map showing the sampling sites for the mercury bioavailability study. The map key shows the symbol defining each sampling type.

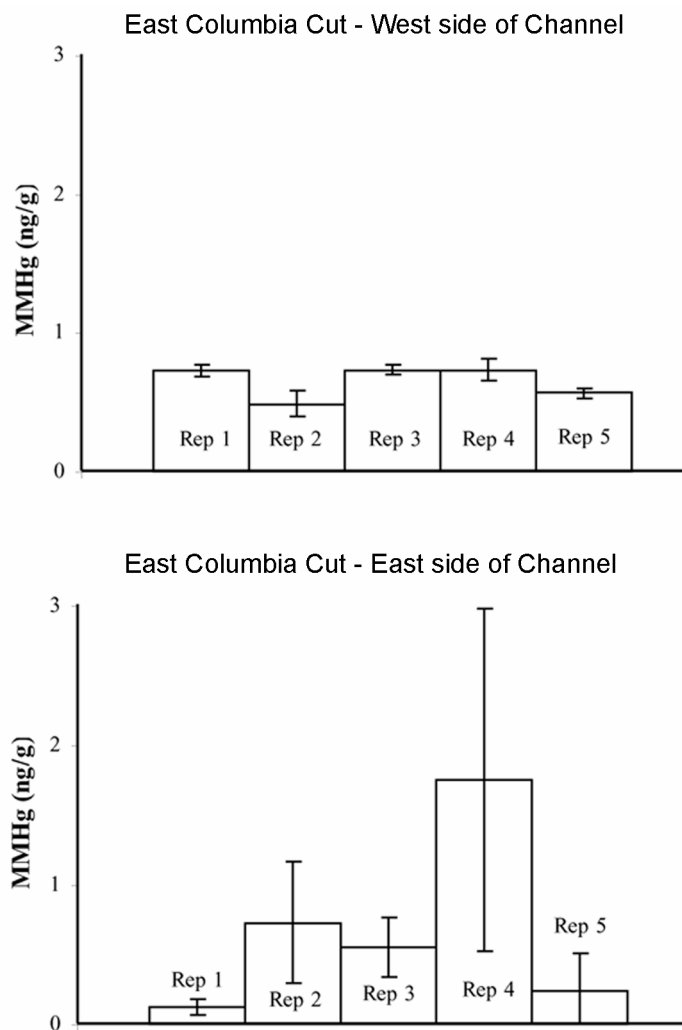


Figure 7. Small scale variation in methyl mercury concentrations at East Columbia Cut in the central Bay-Delta. Field Replicates are shown with error bars as the standard deviation of analytical triplicates.

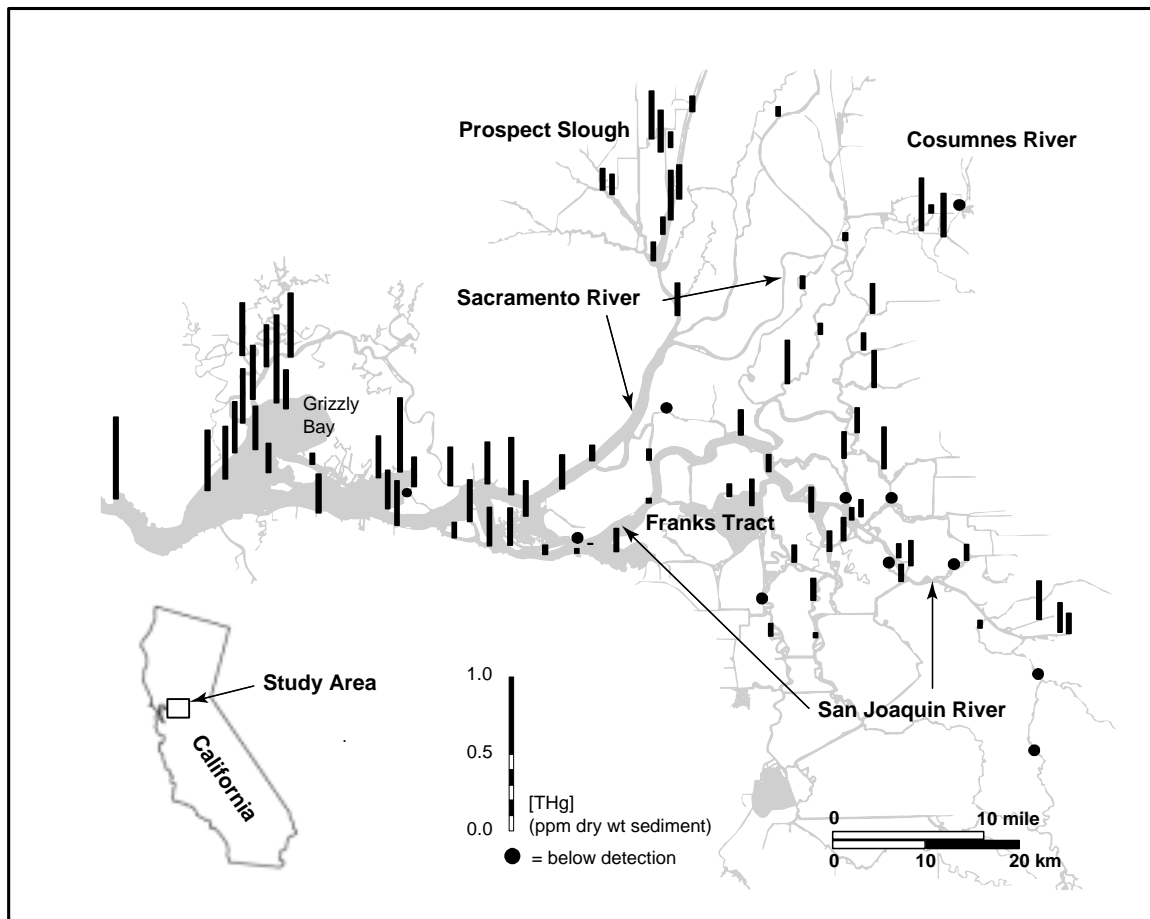


Figure 8. Total mercury surficial (0-0.5 cm) sediment concentration for locations within the Delta and surrounding tributaries and bays. Mercury concentration for each location sampled is represented by a scale bar and the key is given in ppm dry weight sediment. Sampled locations with mercury values less than the method detection limit of 0.10 ppm are represented by solid black circles.

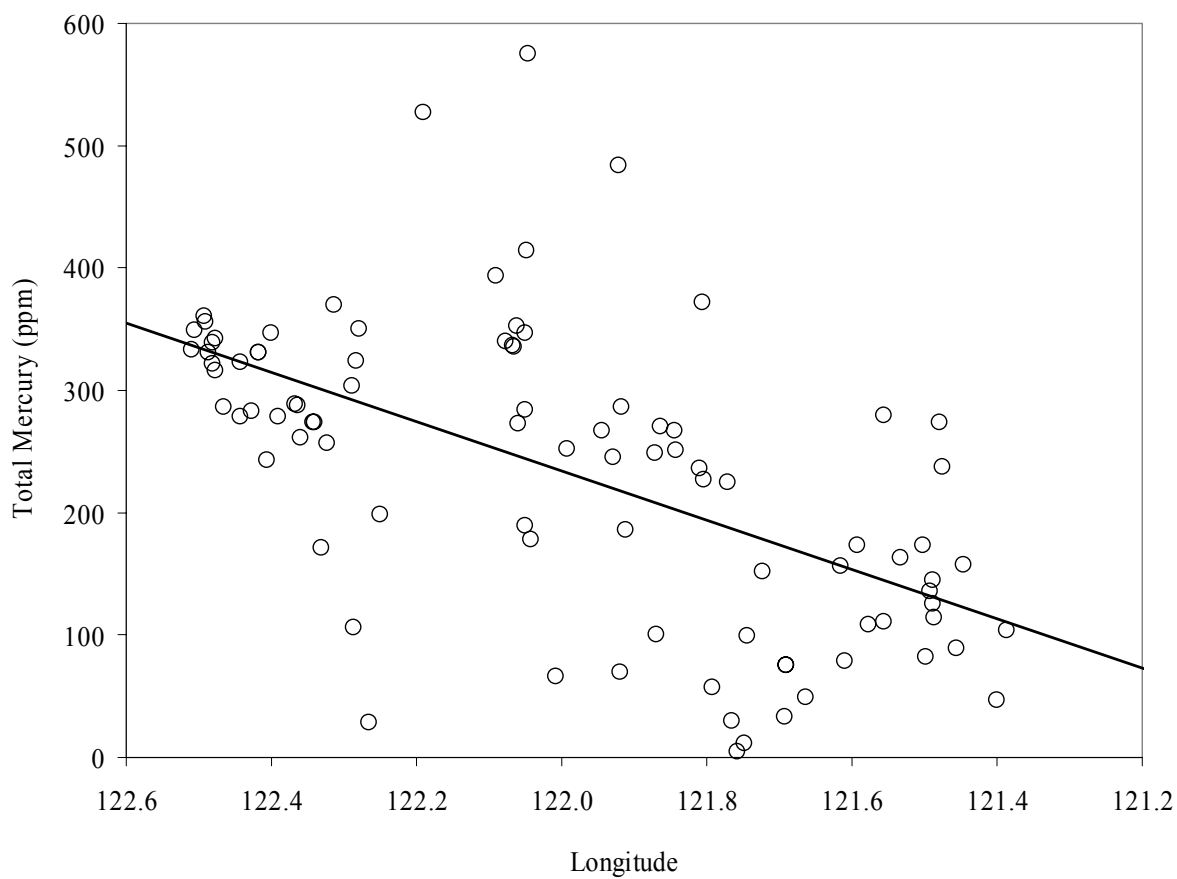


Figure 9. Correlation between total mercury concentration and longitude ($R^2 = 0.34$) for samples collected from the Bay-Delta between 38.00° and 38.15° latitude.

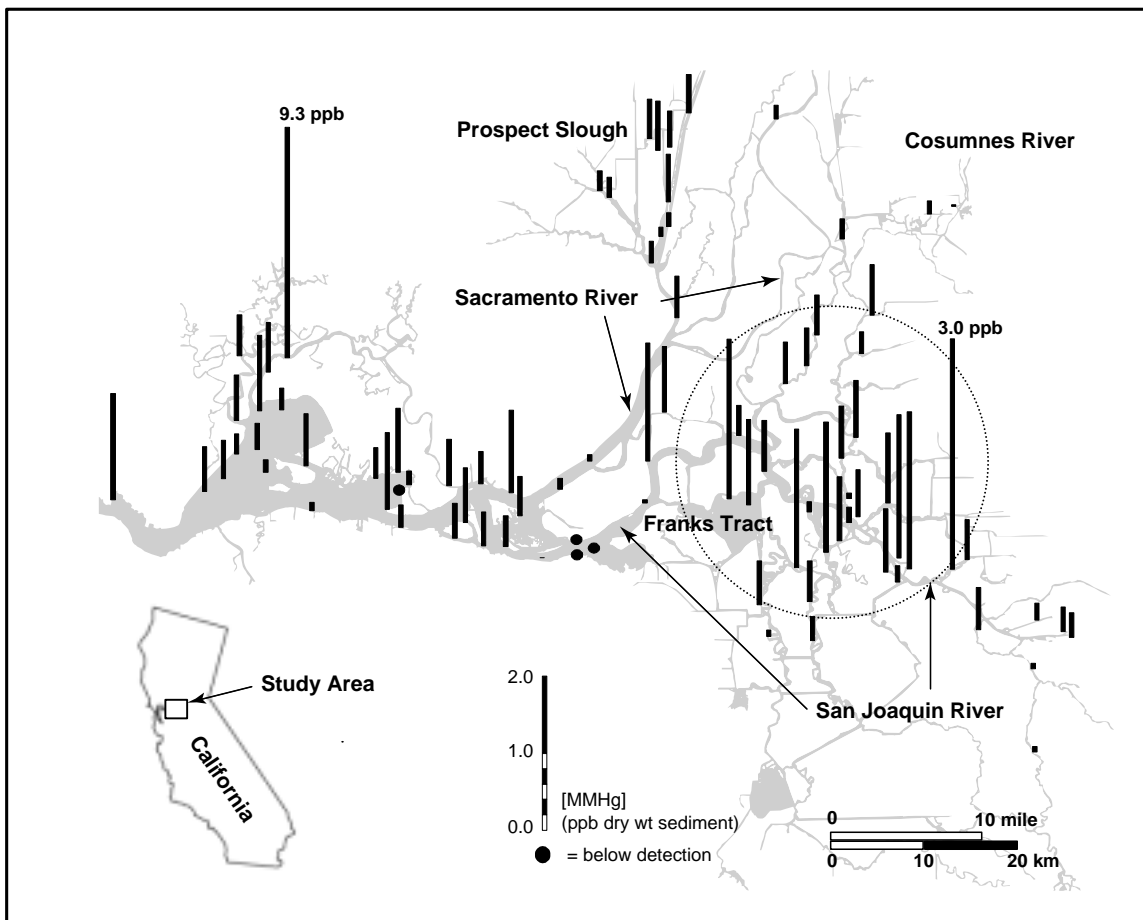


Figure 10. Methyl mercury surficial (0-0.5 cm) sediment concentration for locations within the Delta and surrounding tributaries and bays. Methyl mercury concentration for each location sampled is represented by a scale bar and the key is given in ppb dry weight sediment. Two sites are shown with the methyl mercury concentrations explicitly expressed (in ppb) as the concentration of methyl mercury was large in comparison to all other samples. Sampled locations with methyl mercury values less than the method detection limit of 0.019 ppb are represented by solid black circles. The dashed line circle represents the approximate boundary of the study area operationally defined as the “central delta”.

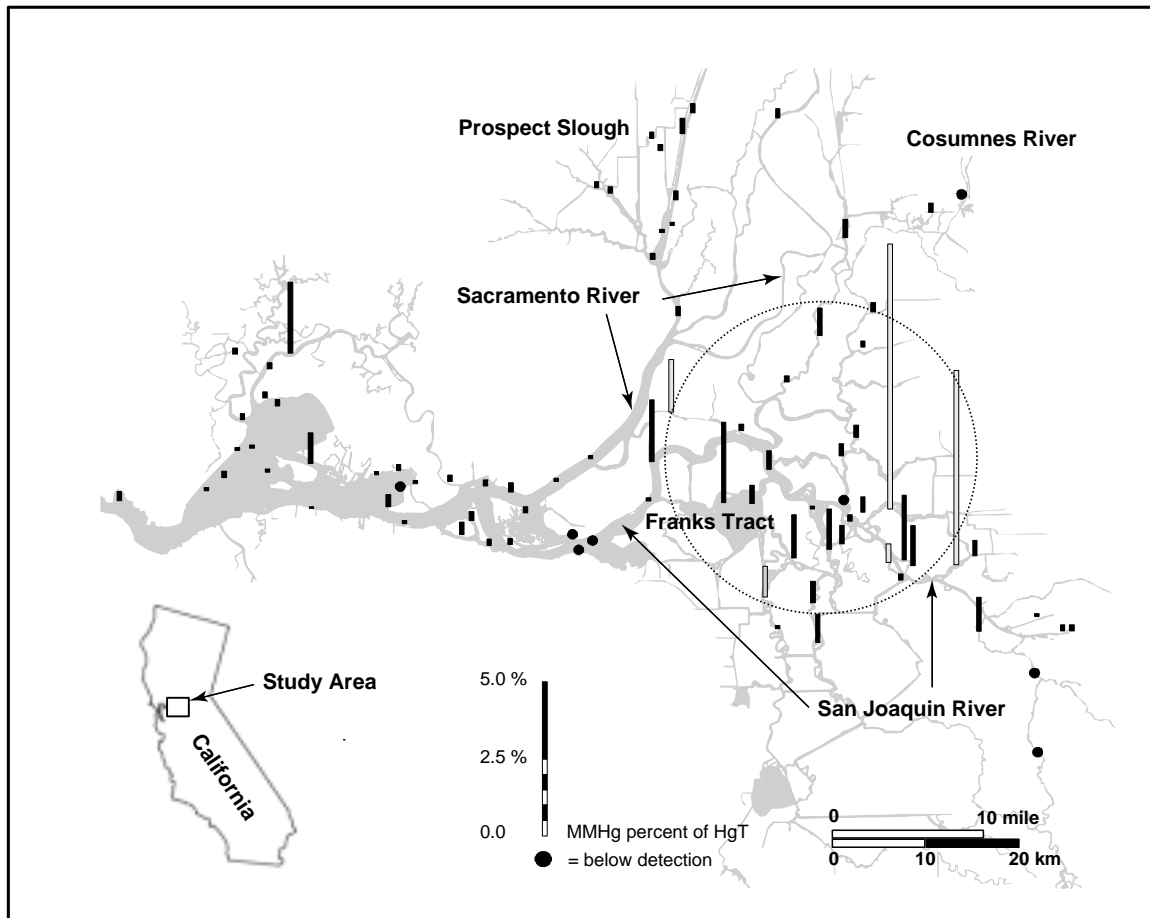


Figure 11. Methyl mercury to total mercury ratios (as a percent) in surficial (0-0.5 cm) sediment for locations within the Delta and surrounding tributaries and Bays. Grey scale bars are indicative of an upper limit ratio, as the methyl mercury to total mercury ratio was calculated using the method detection limit for total mercury. Solid black circles were used to indicate locations with methyl mercury values and total mercury values less than method detection limits. The dashed line circle represents the approximate boundary of the study area operationally defined as the "central delta".

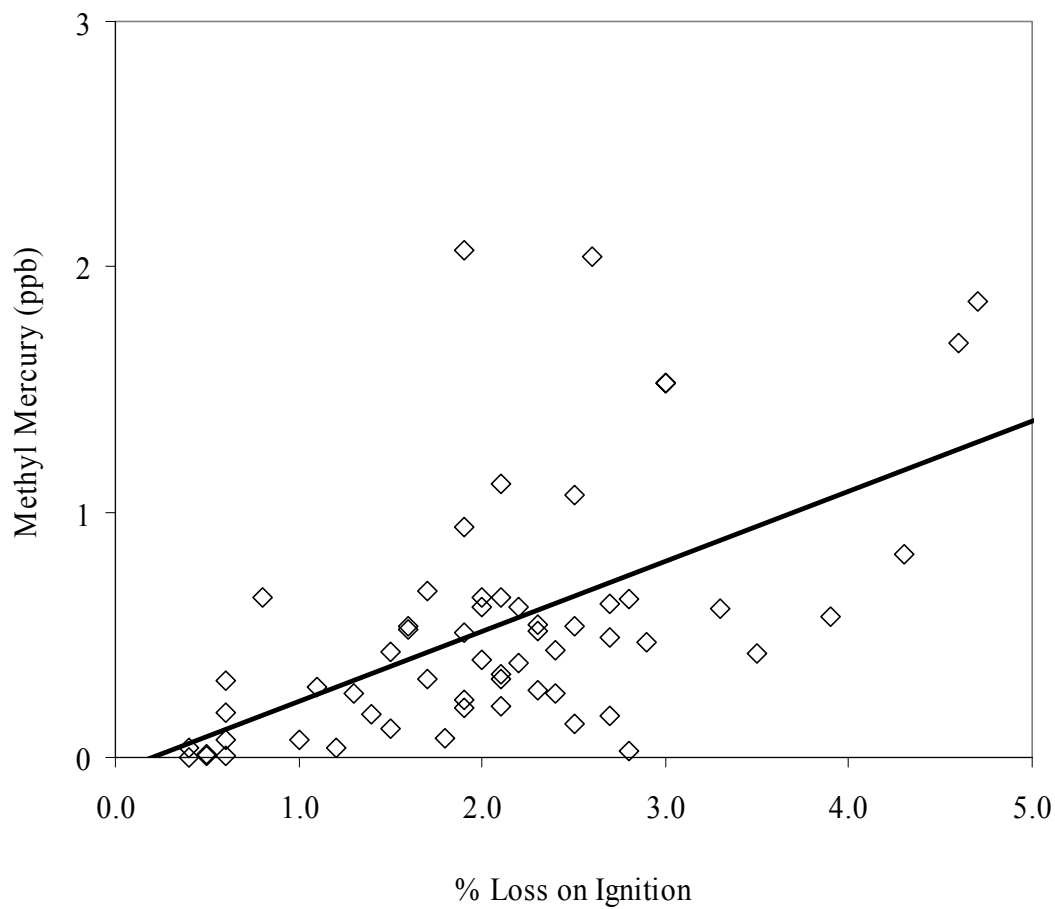


Figure 12. Correlation between methyl mercury and percent loss on ignition in Delta sediment samples collected during the winter of 1999 ($R^2 = 0.32$).

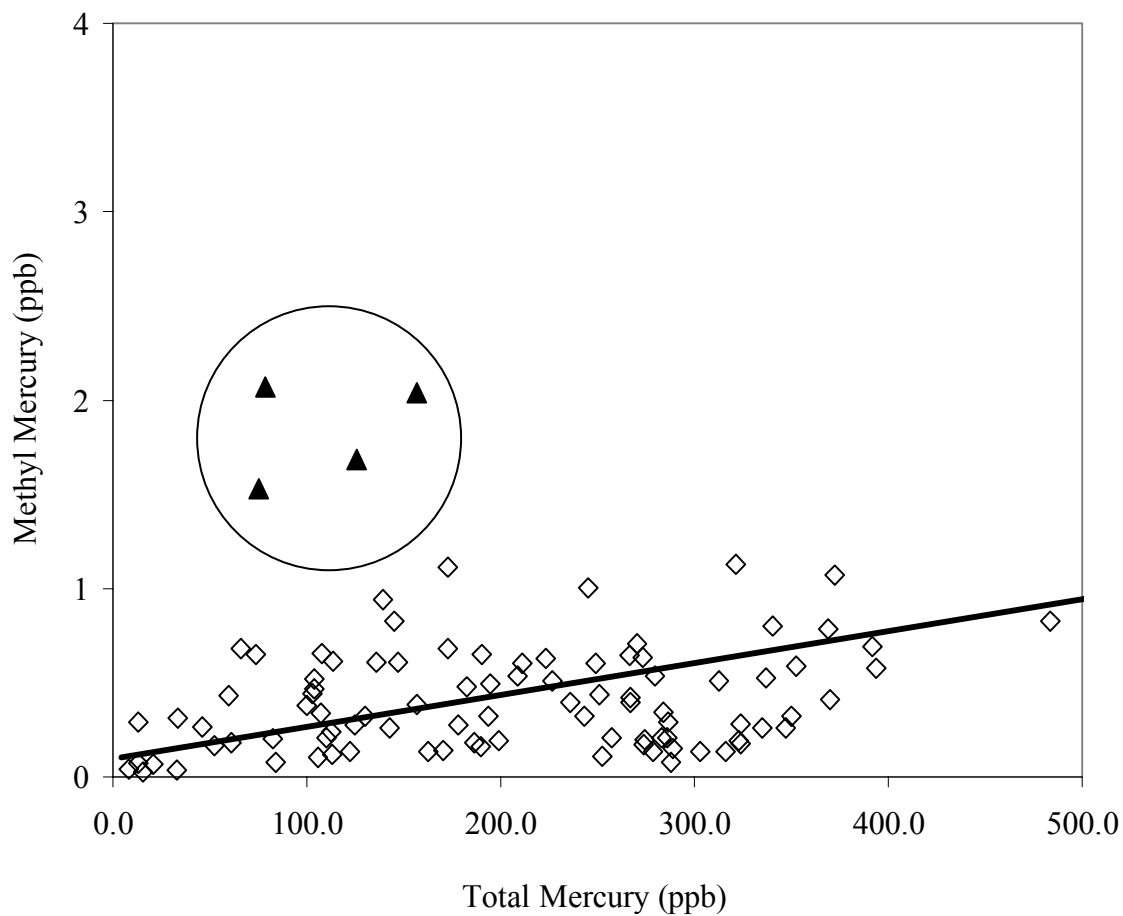


Figure 13. Correlation between methyl mercury and total mercury in Delta sediment samples collected during the winter of 1999 ($R^2 = 0.19$). Circled triangles were considered as outliers and were left out of the correlation analysis.

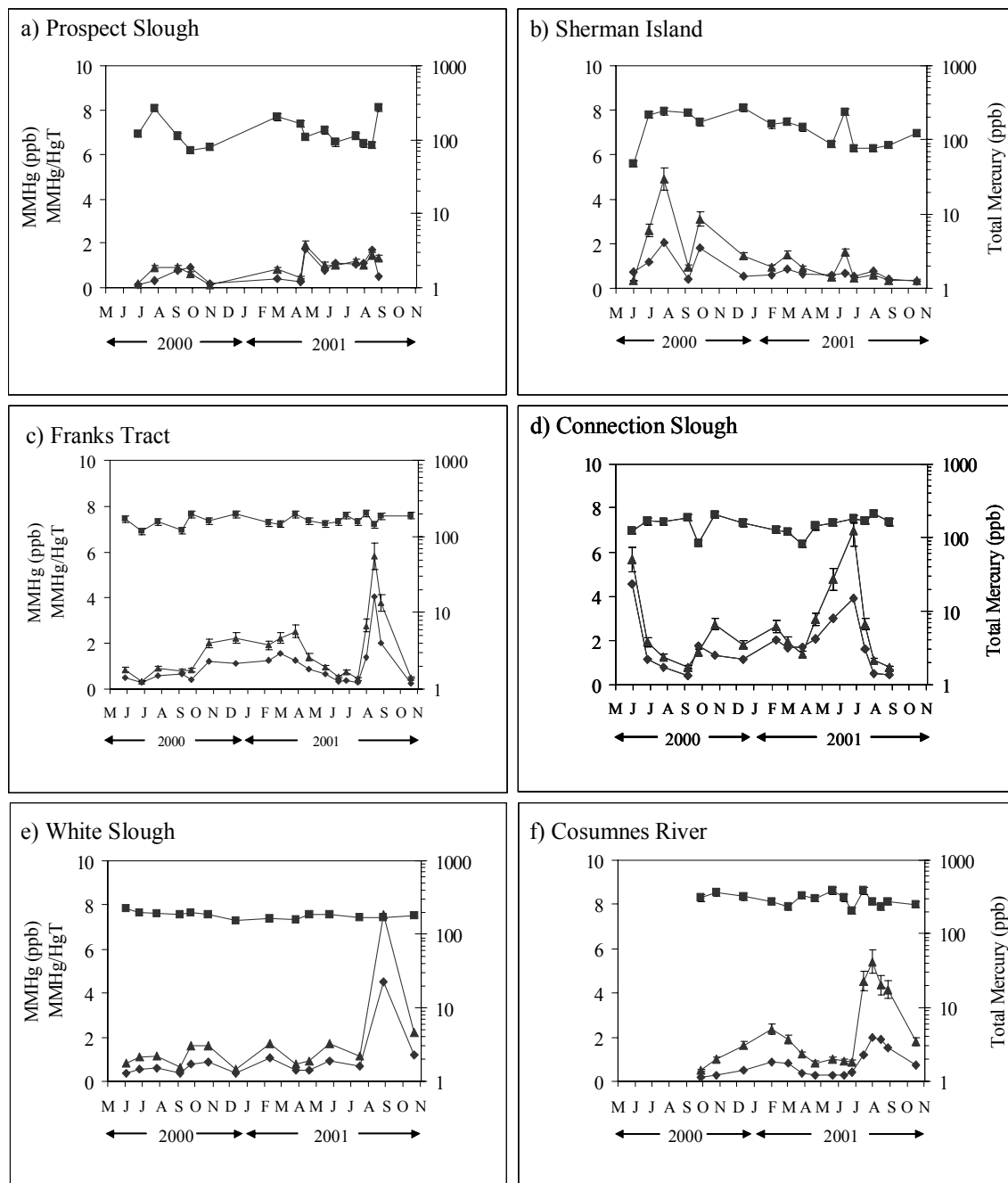


Figure 14. Seasonal changes in methyl mercury (▲), total mercury (■), and the methyl mercury to total mercury ratio (as a percent)(◆) in surficial sediment (0-0.5 cm) of the Bay-Delta. Methyl mercury (ppb) and methyl mercury to total mercury ratio (as %) share the primary y-axis. Total mercury is on the second y-axis (log scale). Error bars represent analytical uncertainty rather than field duplication.

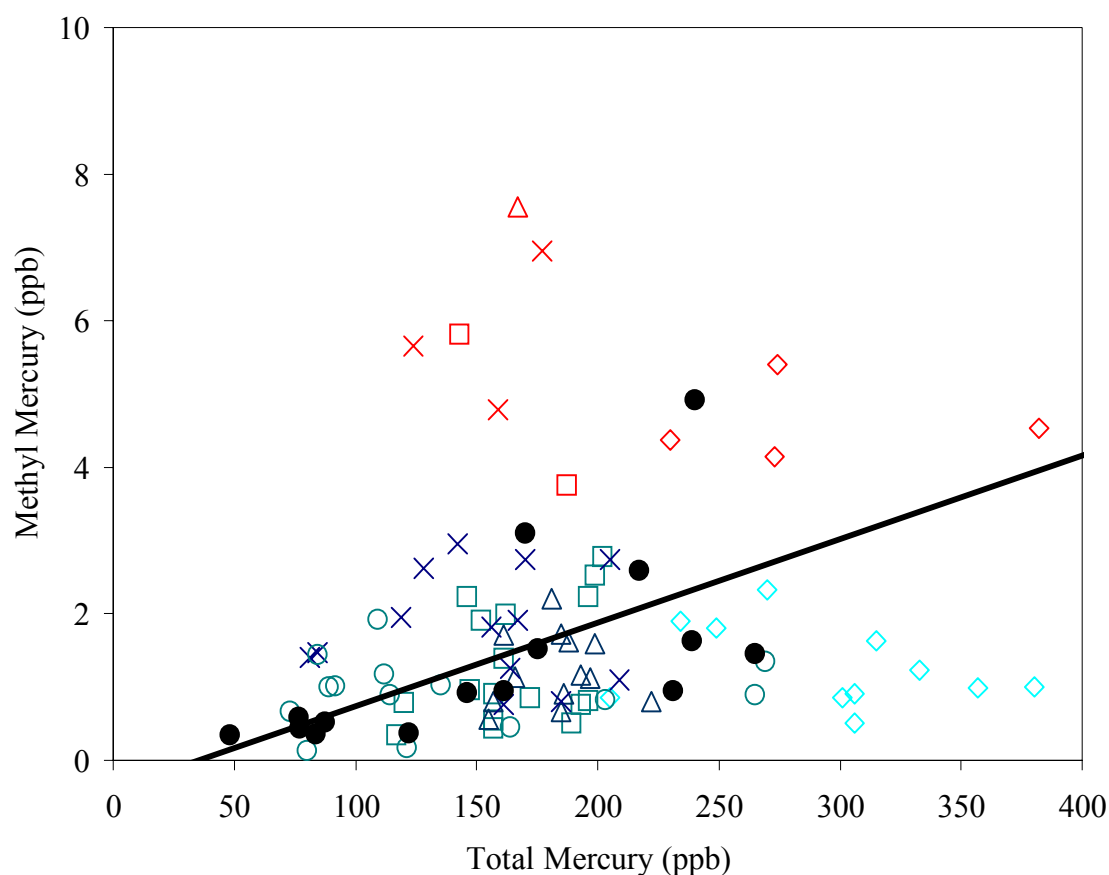


Figure 15. Methyl mercury and total mercury concentration of surficial sediment samples collected at Franks Tract (□), White Slough (Δ), Connection Slough (x), Prospect Slough (○), Cosumnes River (◇), and Sherman Island (●). Red markers indicate samples collected during the seasonal peak of *in situ* methyl mercury production. A positive correlation between methyl mercury and total mercury is shown only for samples collected at Sherman Island (regression coefficient of $R^2 = 0.40$).

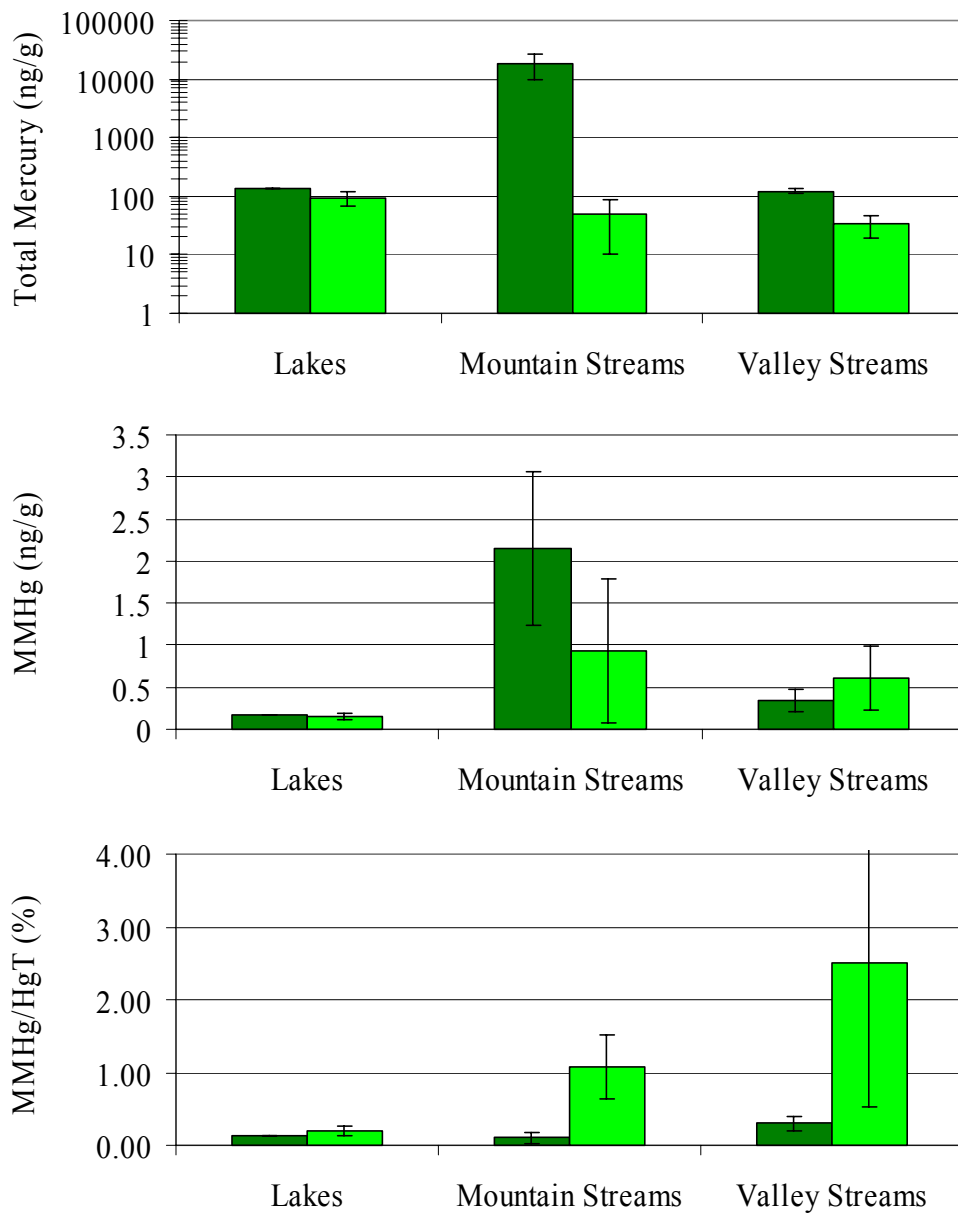


Figure 16. Three panels showing total mercury concentration, methyl mercury concentration, and the methyl mercury to total mercury ratio (as a percent) in unsieved surficial sediments collected from coastal and Sierra lakes, mountain streams, and valley streams. Dark colored bars are from the coastal range and light colored bars are from the Sierra range. Each bar is the averaged value of many locations within a particular classification. The error bars are the standard error of samples within a particular classification.

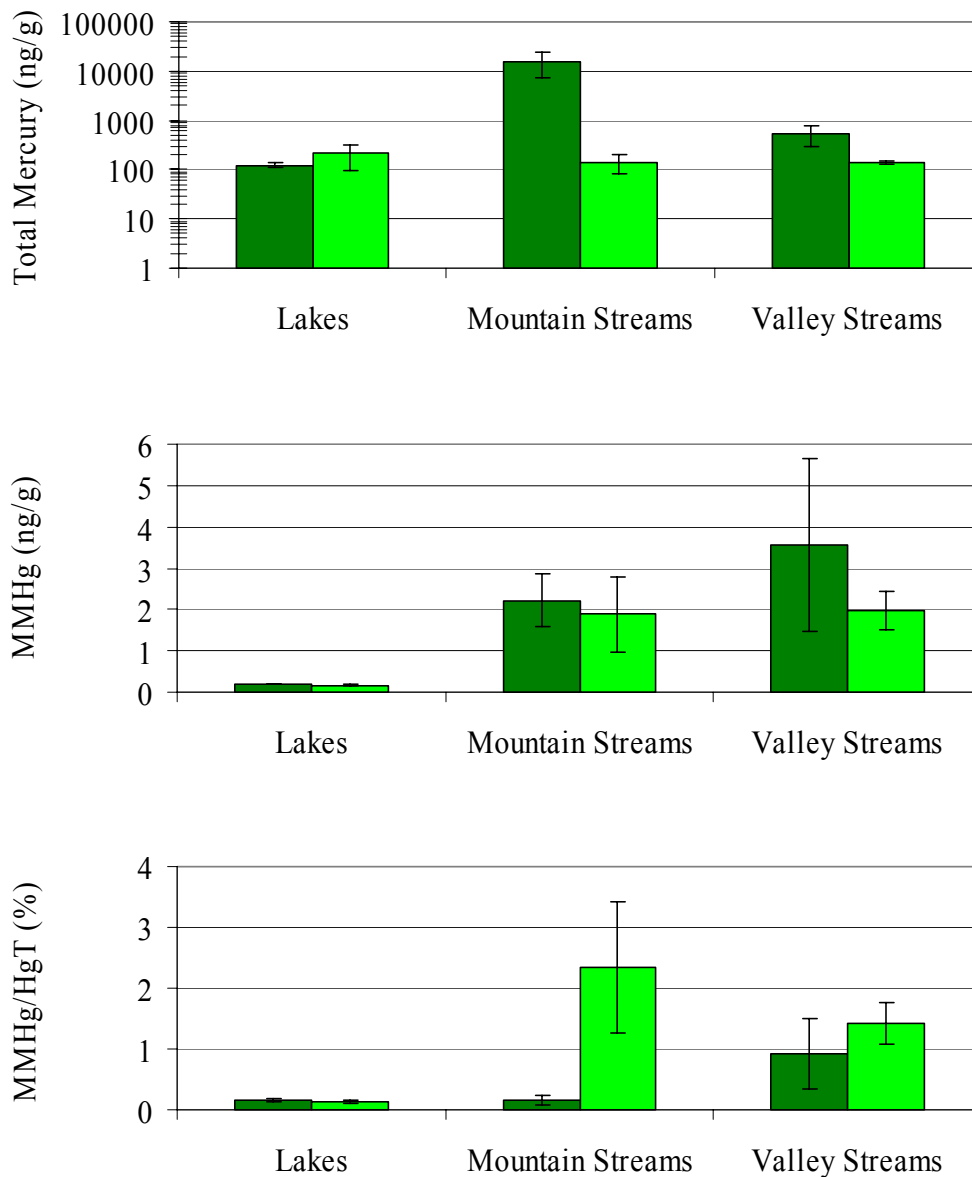


Figure 17. Three panels showing total mercury concentration, methyl mercury concentration, and the methyl mercury to total mercury ratio (as a percent) in sieved surficial sediments collected from coastal and Sierra lakes, mountain streams, and valley streams. Dark colored bars are from the coastal range and light colored bars are from the Sierra range. Each bar is the averaged value of many locations within a particular classification. The error bars are the standard error of samples within a particular classification.

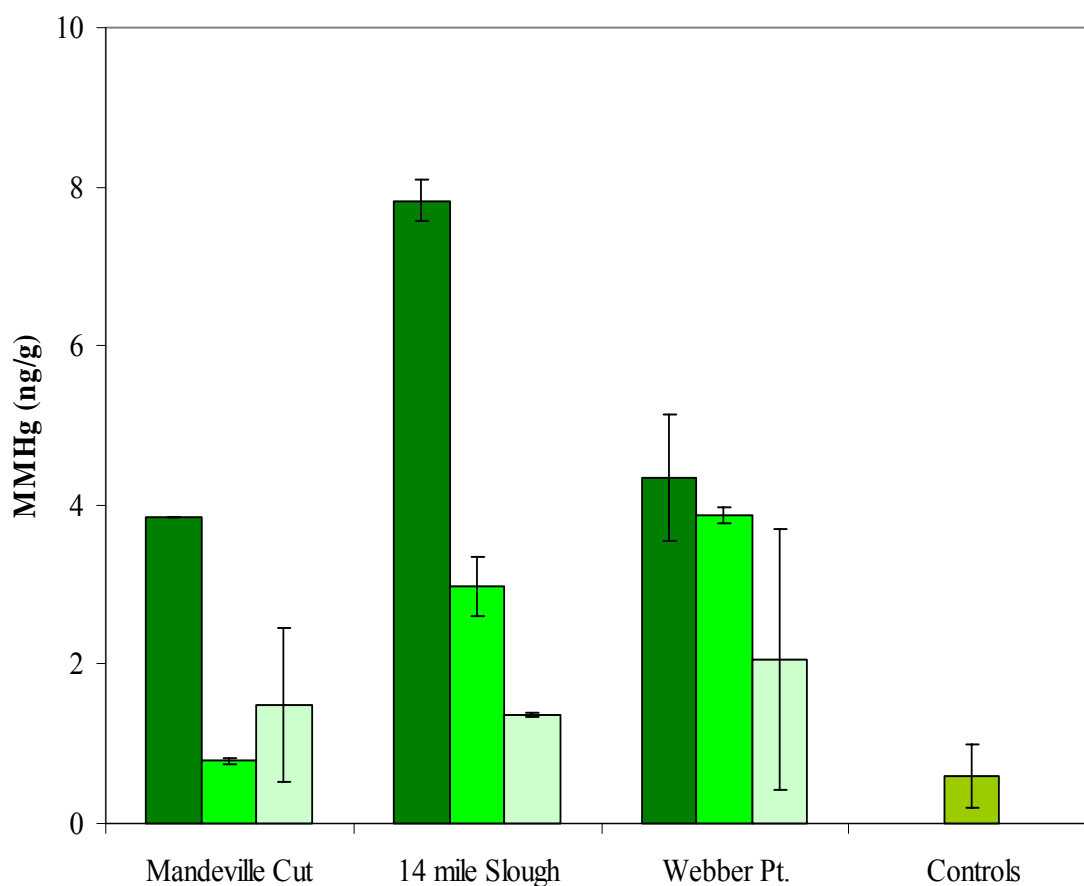


Figure 18. Methyl mercury concentrations in surficial sediments collected from three wetland areas and one control area outside the wetland area. Dark colored bars are from the interior of the wetlands, medium colored bars are mid way between the interior and fringe of the wetland, and the light colored bars are from the outer fringe of the wetland areas. The bars represent the average of field duplicates and the error bars are the range of field duplicates.

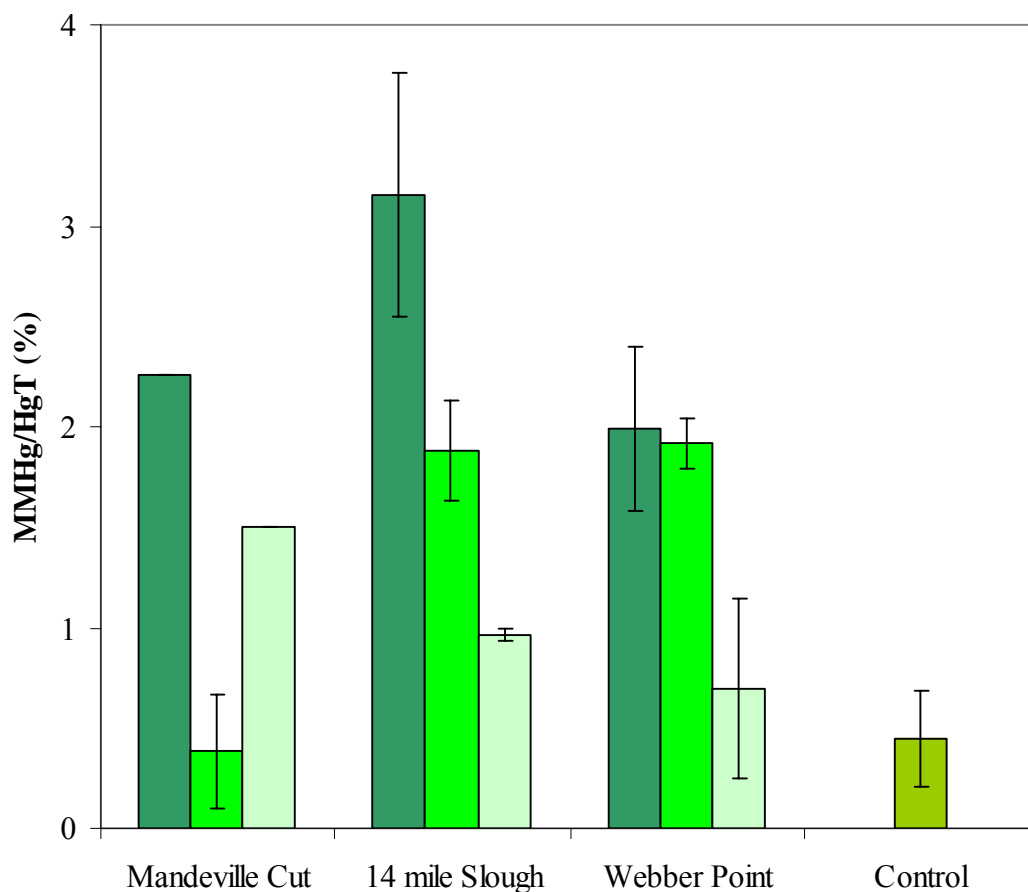


Figure 19. Methyl mercury to total mercury ratio as a percent in surficial sediments collected from three wetland areas and one control area outside the wetland area. Dark colored bars are from the interior of the wetlands, medium colored bars are mid way between the interior and fringe of the wetland, and light colored bars are from the outer fringe of the wetland areas. The bars represent the average of field duplicates and the error bars are the range of field duplicates.